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A Comparison of Some Physical Properties of Hydrogen and Deuterium Bromides

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The absorption spectra and vapor pressures of the hydrogen and deuterium bromides have been measured. The frequency difference between the absorption curves of these compounds is about three times as great as can be accounted for by the zero-point energy differences. Theoretical reasons for this effect are discussed. The vapor pressures are almost identical. The application of Trouton's rule to isotopic compounds is discussed and calculated values for the constant are presented.

INVESTIGATIONS which have been reported from this laboratory[1] show that the replacement of the hydrogen in hydrogen iodide by deuterium leads to higher vapor pressures, a lower melting point and a lower boiling point. These changes are of the same sign as those which have been noted by Claussen and Hildebrand[2] for the hydrogen fluorides and opposite to those noted for the corresponding chlorides.[3] The bromides furnish examples which are intermediate between the chlorides and iodides. The vapor pressures of deuterium and hydrogen bromides are practically the same, the boiling points are almost identical and only in the case of the triple point is a definite difference noted, the deuterium bromide having the slightly higher melting point.

The bromides were prepared by passing a mixture of bromine and hydrogen or deuterium over a heated platinum spiral in a manner similar to that used for the preparation of the iodides. The halides were each fractionally distilled three times and the middle fraction was finally sealed in a unit which included a quartz cell by means of which the absorption spectra were ascertained, a quartz spiral manometer for measurements of the vapor pressure and a cell in which the halide was condensed and in which a five-junction copper constantan thermocouple had been inserted.

A comparison of the absorption spectra of the hydrogen and deuterium halides gives an insight into the nature of the energy levels involved. The continuous absorption of the hydrogen iodides sets in at a frequency about equivalent to the energy of dissociation while that of the bromides begins at a frequency corresponding to an energy some 10 to 15,000 calories greater than the dissociation energy, assuming an excited halogen atom as one of the products. The striking difference between the absorption spectra of the bromides (Table I and Fig. 1) and those of the iodides is the persistence for the bromides of large frequency differences even at high values of the absorption coefficient, α_ν.

In the case of the iodides the separation of the points of equal absorption began at about 1000

[1] Bates, Halford and Anderson, J. Chem. Phys. **3**, 415 (1935).
[2] Claussen and Hildebrand, J. Am. Chem. Soc. **56**, 1820 (1934).
[3] Lewis, Macdonald and Schutz, J. Am. Chem. Soc. **56**, 494 (1934).

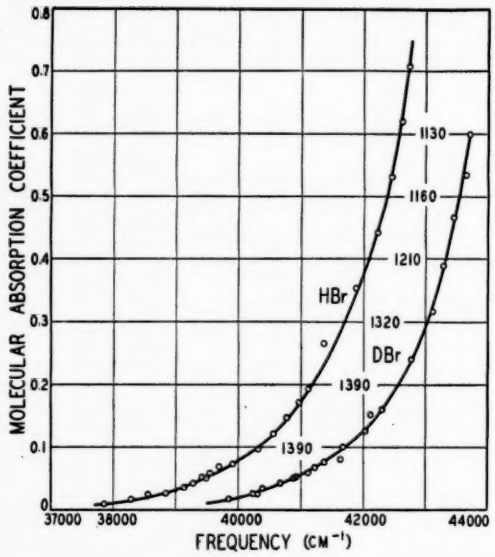

FIG. 1.

cm^{-1} and gradually approached the difference in zero-point energy (340 cm^{-1}) at high values of α_v. The bromides, however, have a separation of 1100 cm^{-1}, almost three times the zero-point energy difference (374.8 cm^{-1}) at the highest values of α_v measured. This phenomenon is predictable from the relation of frequency of absorption with the frequency corresponding to dissociation (33,200 cm^{-1}). Absorption to portions of a repulsive upper potential energy curve which lies considerably above the energy of dissociation would always be altered by two factors when hydrogen is replaced by deuterium: first the difference in zero-point energy, and second the contraction of the eigenfunction to smaller values of internuclear separation. The second factor would be practically eliminated in the case where the upper curve is becoming asymptotic to the dissociation level and hence the separation of the absorption curves of the hydrogen and deuterium compounds would tend to approach the zero-point energy difference as was observed in the case of the iodides. The data presented in this paper indicate that the second factor enters to a marked extent in the bromides.

One interesting result of these studies is that it is possible to produce by illumination known amounts of hydrogen atoms in a mixture of hydrogen and deuterium iodides and measure the relative efficiencies of the reactions H+HI and H+DI. Such studies are under way in this laboratory.

TABLE I.

FREQUENCY (mm^{-1})	LOG MOLE ABS. COEFF.	FREQUENCY (mm^{-1})	LOG MOLE ABS. COEFF.
Hydrogen bromide			
3785	0.009	4033	0.097
3828	.017	4056	.121
3855	.024	4077	.146
3884	.025	4098	.170
3913	.035	4112	.194
3928	.042	4137	.265
3948	.049	4189	.353
3941	.051	4223	.441
3955	.059	4246	.531
3970	.068	4261	.619
3992	.073	4273	.708
Deuterium bromide			
3985	0.017	4168	0.100
4030	.025	4202	.126
4022	.025	4211	.151
4039	.034	4230	.160
4067	.042	4278	.240
4090	.050	4313	.316
4092	.051	4328	.389
4111	.059	4345	.466
4122	.068	4365	.535
4137	.075	4370	.598
4163	.080		

THE VAPOR PRESSURES OF HYDROGEN AND DEUTERIUM BROMIDES

The experimental arrangement employed for the measurement of the vapor pressures has already been described. The thermocouple was imbedded in a tube which was sealed into the apparatus in such a way that its lower two inches were immersed directly in the bromide. The cell containing the bromide was in turn immersed in an ether bath in a vacuum flask. Nitrogen cooled by passing through liquid air was directed through a coil of lead tubing immersed in the ether bath. In order to maintain uniform temperature, a rapid stream of cooled air was bubbled through the bath. The required nitrogen stream was sufficiently rapid to permit close regulation of the temperature throughout the period of measurement. With this arrangement, vapor pressures could be obtained with a quantity of the bromide sufficient to permit the measurement of the triple point by means of a heating curve.

The boiling points and triple points are given in Table II.

TABLE II.

	B. p.		Tr. p.
HBr	206.3		186.2
	206.38	Giauque and Wiebe	186.24
DBr	206.3		185.7

TABLE III. *Vapor pressure of hydrogen bromide.*

T	log p (exp.)		log p (calc.)
		liquid	
198.6	2.704		2.703
191.05	2.514		2.515
186.65	2.398		2.398
		solid	
184.9	2.340		2.344
180.3	2.192		2.191
174.15	1.955		1.975

TABLE IV. *Vapor pressure of deuterium bromide.*

T	log p (exp.)		log p (calc.)
		liquid	
205.43	2.861		2.861
202.45	2.792		2.792
197.6	2.675		2.676
192.9	2.556		2.558
189.4	2.468		2.467
186.85	2.399		2.398
		solid	
184.7	2.333		2.334
180.3	2.187		2.188
173.9	1.964		1.963

The experimentally determined vapor pressures are expressed by the following equations:

$$\log p(\mathrm{HBr})(l) = 7.465 - 945.7/T, \quad (1)$$
$$\log p(\mathrm{DBr})(l) = 7.517 - 956.5/T, \quad (2)$$
$$\log p(\mathrm{HBr})(s) = 8.309 - 1103/T, \quad (3)$$
$$\log p(\mathrm{DBr})(s) = 8.306 - 1103/T. \quad (4)$$

The character of the data is shown in Tables III and IV, for the hydrogen and deuterium bromide, respectively, by comparison of the experimental points with the corresponding calculated values, using the above equations.

Eq. (1) agrees, within experimental error, with the equation for liquid hydrogen bromide given in *International Critical Tables*[4] and deviates only slightly from an equation based upon the boiling point and calorimetric measurements of Giauque and Wiebe (Eq. (5)).[5]

$$\log p(\mathrm{HBr})(l) = 20.179 - 4.672 \log T - 1338/T. \quad (5)$$

[4] Int. Crit. Tab. **3**, 213.
[5] Giauque and Wiebe, J. Am. Chem. Soc. **50**, 2193 (1928).

Some difference in the latter comparison is to be expected, because no account has been taken of the deviations from the ideal gas laws.

The new data for solid hydrogen bromide are slightly less satisfactory, and the principal factor in fixing the constants of Eq. (3) has been the necessity for equal vapor pressure of the solid and liquid at the triple point, a factor which apparently was overlooked in deriving the corresponding equation for the *International Critical Tables*. Eq. (3) is also in better agreement with the heat of sublimation given by Giauque and Wiebe, if account is taken of the probable magnitude of deviations from the ideal gas law. Eq. (6), based on the data of Giauque and Wiebe, is included for comparison.

$$\log p(\mathrm{HBr})(s) = 10.488 - 0.004084T - 0.2766 \log T - 1250/T. \quad (6)$$

From Eq. (1), the average heat of vaporization of the liquid, assuming the ideal gas law, is 4330 cal. An approximation to the value at the boiling point may be obtained by subtracting the product of half the temperature range by the average heat capacity difference between the vapor and the liquid. The result is 4257 cal. as compared with 4210 cal. found by Giauque and Wiebe.

The heat of vaporization of deuterium bromide is obtained by multiplying 4210 by the ratio of the two values based upon vapor pressure measurements, with 4258 cal. as the result.

TROUTON'S RULE FOR ISOTOPIC SUBSTANCES

The relation between the heat of vaporization and the absolute temperature known as Trouton's rule would be expected to be obeyed by two isotopic substances with greater exactness than by most compounds. However, even a cursory examination of the data obtained to date shows that there exist considerable deviations from the rule even when pairs of isotopic substances are compared. Thus Urey and Teal[6] have shown that the vapor pressure curves of corresponding liquid hydrogen and deuterium compounds intersect at some temperature which is usually not far from the normal boiling point. At the point of intersection, since the heats of

[6] Urey and Teal, Rev. Mod. Phys. **7**, 34 (1935).

TABLE V.

SUBSTANCE	a	b	$\Delta H/T_b$	SUBSTANCE	a	b	$\Delta H/T_b$
NH_3	8.1616	1266.08	24.179	HF	6.3739	1316.8	20.551
ND_3	8.2800	1308.23	24.721	DF	6.2026	1261.6	19.766
H_2O	9.1582	2342.5	28.742	HCl	7.6192	891.30	21.696
D_2O	9.2854	2399.1	29.325	DCl	7.6125	906.59	21.665
HCN	7.795	1467	22.171	HBr	7.465	945.7	20.397
DCN	7.695	1440	21.728	DBr	7.517	956.5	20.630
				HI			19.869
				DI			19.932

vaporization are not equal, Trouton's rule is not obeyed. To test this further, the constant was calculated for each of a group of substances and these constants are presented in Table V.

The constants a and b are those giving the vapor pressure according to Eq. (7).

$$\log P_{(\text{mm})} = a - b/T \tag{7}$$

where $b = \Delta H/4.5787$. Correction to constant vapor concentration, as in the Hildebrand[7] modification, produces changes too small to alter the conclusion. For example, the difference between the Trouton's constants for the chlorides is increased in this manner by 0.03.

An interesting observation to be made from Table V is that an isotopic change produces the greatest shift in the value of the constant for those substances which are known to deviate most from Trouton's rule, water and ammonia.

[7] Hildebrand, J. Am. Chem. Soc. **37**, 970 (1915).

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Comparison of the Raman Spectra of 1,1,1- and 1,1,2-Trichloroethane

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The Raman frequencies of 1,1,1- and 1,1,2-trichloroethane have been obtained. Comparison with CCl_4 indicates that the Cl_3C and Cl_2HC radicals have tetrahedral symmetry. The frequencies of $Cl_3C \cdot CH_3$ and $Cl_2HC \cdot CH_2Cl$ are compared, and the combination frequencies and modes of vibration of the two molecules indicated.

THE Raman spectra of 1,1,1- and 1,1,2-trichloroethane have been up to the present time unknown. Among the compounds examined by Hanle,[1] are listed the Raman frequencies of $Cl_2C=CHCl$, obviously misnamed trichloroethane. Consequently it has seemed worth while to investigate the Raman spectra of both 1,1,1- and 1,1,2-trichloroethane, and to compare them with those of similar compounds.

Apparatus and experimental technique employed were similar to those described by Wood.[2] In the preliminary investigations a Hilger constant deviation spectrograph was used, having a dispersion of 25A/mm at λ4500. A Cooper-Hewitt Hg arc operated at 750 watts served as light source. The line chosen for excitation was λ4358. A filter consisting of a water solution of $NaNO_2$ was used to eliminate λ4047 and λ4078. With this apparatus exposures ranged from 30–60 min. In the later work a spectrograph containing two 60° prisms and having a dispersion of 12A/mm at λ4500 was used. Two low pressure Hg arcs operated at 150 watts each served as light source. This apparatus, however, required exposure from 24 to 96 hours. The 1,1,1- and 1,1,2-trichloroethane were purchased from the Eastman Kodak Company and were fractionally distilled before use. The boiling range for the distilled $Cl_3C \cdot CH_3$ was 74° to 75.5°C and for the distilled $Cl_2HC \cdot CH_2Cl$ was 113° to 115°C, both at normal pressure. Both compounds decompose very slowly when exposed to light, necessitating redistillation half-way through each exposure. Measurements were made directly on the spectrograms and also on microphotometer traces (Koch-Goos). A Cu arc spectrum was used for comparison, and wavelengths of the Raman lines were calculated by the Hartmann formula.

[1] W. Hanle, Ann. d. Physik, [5] **15**, 345 (1932).
[2] R. W. Wood, Phil. Mag. [7] **6**, 729 (1928); Phys. Rev. **36**, 1421 (1930).

TABLE I. *1, 1, 1-trichloroethane.*

241 (7)*	714 (7b)	1242 (½b)	1592 (½b)
345 (10)*	{1071 (2)	{1361 (½)	2743 (½b)
	{1086	{1384 (½)	
523 (9)*	1175 (1)	{1424 (2)	2943 (7)
		{1451	3011 (6)

TABLE II. *1, 1, 2-trichloroethane.*

255 (4)*	525 (1)	1056 (1b)	1575 (½b)
283 (2)*	638 (3)	1207 (2)	2960 (8)
332 (10)*	664 (5b)	1260 (2)	2996 (7)
395 (3)*	{772 (10)	1304 (2)	3021 (5b)
	{781		
441 (½)*	931 (1)	1428 (2)	

* Observed also as anti-Stokes lines.

In Tables I and II are tabulated the Raman frequencies in wave numbers for 1,1,1- and 1,1,2-trichloroethane. The numbers in parentheses are the relative intensities, obtained from the microphotometer traces.

DISCUSSION

The striking resemblance between the first four Raman frequencies of $Cl_3C \cdot CH_3$ and CCl_4 indicates that the Cl_3C radical also has tetrahedral symmetry. Consequently the frequency 241 can be ascribed to a bending of the C−Cl bond and 523 to an expansion and contraction of the Cl_3C radical as a whole. The frequency 714 does not correspond, however, to the doublet 760,793 of CCl_4. Following the method of Dadieu and Kohlrausch in calculation,[3] it is found that the frequency of vibration along the C−C bond between Cl_3C and CH_3 is 680. The frequency 714 must then be due to a stretching of this bond. A similar calculation for $Cl_2HC \cdot CH_2Cl$ gives a frequency of 443 which may be compared with the Raman frequency 441. This line is very weak, however. It is possible that the selection rules for $Cl_2HC \cdot CH_2Cl$ are such that the frequency 441 cannot give rise to a strong Raman line unless in combination with some other frequency. It may be noted that 332+441=773 is nearly the mean of the doublet 772,781 (10). Since each radical in $Cl_3C \cdot CH_3$ is symmetrical, one would expect numerous instances of degeneracy which would not occur in $Cl_2HC \cdot CH_2Cl$. Consequently $Cl_2HC \cdot CH_2Cl$ should have more lines in its Raman spectrum than $Cl_3C \cdot CH_3$, as is found to be the case. A comparison of the Raman spectra of the two compounds is given in Table III, possible combination frequencies being indicated, as well as the modes of vibration responsible for certain lines.

[3] A. Dadieu and K. W. F. Kohlrausch, Monatsh. f. Chem. **52**, 396 (1929).

TABLE III.

$Cl_3C \cdot CH_3$			$Cl_2HC \cdot CH_2Cl$	
RAMAN	COMBINATION	MODE OF VIBRATION	RAMAN	COMBINATION
241(7)		C−Cl bending	255(4)	
345(10)			332(10)	
523(9)		Cl_3C and Cl_2HC expansion and contraction	525(1)	
714(7b)		C−C stretching	441(½)	
			664(5b)	2(332)
{1071(2)	345+714		{772(10)	332+441
{1086			{781	
			1056(1b)	2(525)
1242(½b)	523+714			
{1361(½)	345+2(523)			
{1384				
{1424(2)	2(714)	C−H bending	1428(2)	
{1451				
1592(½b)	3(523)		1575(½b)	3(525)
2743(½b)	2[345+2(523)]			
2943(7)		C−H stretching	2960(8)	
3011(6)			2996(7)	
			3021(5b)	

It is interesting to note that the doublet 1424,1451 in the Raman spectrum of $Cl_3C \cdot CH_3$ can be ascribed both to the doubling of the fundamental frequency 714 and to the bending of the C−H bond.

In conclusion the author wishes to express his indebtedness to Professor W. W. Watson for his many helpful suggestions during the course of this work, and to his father under whom the preliminary investigations were carried out at Dartmouth College.

The Ultraviolet Absorption Spectra of Cis- and Transdichloroethylenes

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(Received June 18, 1935)

The absorption spectra of cis- and of transdichloroethylene have been photographed from the visible to 750A. There are continua in the quartz region and at short wavelengths, but discrete bands in the general region of 1300 to 1700A. Two Rydberg series have been found in the cis-form predicting ionization potentials of 9.58 and 9.63 volts. A value in agreement with these figures is found by electron bombardment. No Rydberg series were found in the trans-form, although indications of an ionization potential at about 11.3 volts were obtained by electron bombardment. In both forms the main progressions involve a C=C frequency of about 1400 cm^{-1}, although many prominent differences involving the lowest deformation frequency have been found. A discussion of the various absorption regions has been given, although definite proof of many points must come from other sources.

IN investigating the spectroscopic and photochemical properties of the double bond, it is evident that simple derivatives of ethylene would be advantageous substances with which to work. Olson and Maroney[2] have studied the thermal equilibrium and photochemical steady state for cis- and transdichloroethylenes. The results are in general agreement with a theory of cis-trans isomerization developed by Olson.[3] The photochemical work seems to have been carried out in a region of continuous absorption. It was thought that a complete investigation of the spectra of these two compounds would be of value.

I. EXPERIMENTAL

The two isomers were obtained by fractional distillation of the Eastman product (b.p. 58–61°). This consisted largely of the cis- form, although enough of the trans-form was present for the purpose of the present experiments.

An eight-foot distilling column of the Vigreux type was used for the first separation of the trans-form and for further purification of the cis. The cis-form was distilled until successive fractions gave a constant index of refraction, which required four more distillations than were necessary to give a boiling point constant to 0.1°. Not enough of the transdichloroethylene was obtained to check its purity in this way, but since the first fraction had a smaller boiling range than the cis (0.3°), the same number of distillations was made using a microfractionating column.[4] Just before introducing the materials into the spectrograph small samples were again distilled through this small column, taking the first fraction of the trans- and the last fraction of the cis-dichloroethylene. The boiling points of the samples obtained in this way agreed with those in the literature,[5] 60.1° for the cis- and 47.3° for the transdichloroethylene. The thermometer was calibrated by a Bureau of Standards thermometer and no stem correction was necessary.

A Hilger E-3 spectrograph with quartz train was used for wavelengths greater than 2100A. The hydrogen continuum was used as a source of radiation and a quartz absorption cell 20 cm in length was employed.

For shorter wavelengths a one-meter vacuum grating spectrograph with a dispersion of approximately 8.5A/mm in the first order, was used. The method of using this spectrograph and the light source have been described.[6] Eastman III-0 plates sensitized with Nujol were used for most of the exposures, although Schumann plates were used occasionally, particularly for the extreme ultraviolet.

As wavelength standards the carbon lines at 1548.19 and 1371.28A together with the hydrogen line at 1215.68A in absorption were employed.

The spectrum from the visible to 750A was covered.

The method of measuring the ionization potentials by electron bombardment has been described.[7]

[1] Jesse Metcalf Fellow, 1934–35.
[2] A. R. Olson and W. Maroney, J. Am. Chem. Soc. **56**, 1320 (1934).
[3] A. R. Olson, Trans. Faraday Soc. **27**, 69 (1931).
[4] C. M. Cooper and E. V. Fasce, Ind. Eng. Chem. **20**, 420 (1928).
[5] L. Ebert and R. Büll, Zeits. f. physik. Chemie **A152**, 451 (1931).
[6] W. A. Noyes, Jr., A. B. F. Duncan and W. M. Manning, J. Chem. Phys. **2**, 717 (1934).
[7] W. A. Noyes, Jr., J. Chem. Phys. **3**, 430 (1935).

II. Results

The absorption spectra of the two isomers may be divided roughly into three regions.

(1) There is a region of continuous absorption first observed at low pressures at 1950A for transdichloroethylene and at 1850A for cisdichloroethylene. This region spreads rapidly in both directions as the pressure is increased until at the highest pressures used (188 mm for the cis and 278 mm for the trans) with a path length of 20 cm complete absorption was observed below 2400A. At higher temperatures absorption coefficients have been measured up to 2763A.[2]

On three plates of the cis-form there seemed to be some very diffuse bands underlying the short wave end of this continuum.

(2) The region of discrete absorption extends from 1570A to about 1350A. The bands of the cis-form were shaded toward the violet, while those of the trans-form were shaded toward the red, although sharp band edges were discernible with difficulty except for the most intense bands. Bands of the cis-form were observed to 1340A, while none below 1450A was found for the trans-form. Overlaying the banded absorption of the cis-form was another continuum, first noticeable at low pressures at about 1470A, but increasing in breadth and gradually merging with both the longer and shorter wave continua as the pressure increased.

(3) Below this discrete absorption was a third region of continuous absorption. In the cis-form this appeared to be a true continuum whose center of gravity lies about 78,000 cm^{-1}. In the trans-form there seems to be a series of wide, diffuse bands without structure which gradually merged as the pressure increased.

Table I gives the frequencies of the absorption bands of cisdichloroethylene, together with rough estimates of the intensities based on the appearance of the bands and the pressures at which they were first noticed. Only the discrete bands are included, since the diffuse bands are listed in Table III. The frequencies of the red edges are given. The bands marked *s* were sharper than the others and are probably accurate to about 5 cm^{-1}. The others were more difficult to measure with precision and are probably not reliable to better than 15 cm^{-1}.

Table I. *Discrete bands of cisdichloroethylene (frequencies in wave numbers).*

$\bar{\nu}$	Intensity	$\bar{\nu}$	Intensity	$\bar{\nu}$	Intensity
65016	0	68670	9	72408 (*s*)	7
65164 (*s*)	10	68872	5	72640 (*s*)	8
65260	1	69060	4	72957	7
65352	2	69266	3	73205	1
65737	3	69483	4	73328	5
65845 (*s*)	10	69796	4	73473	0
66020	4	69875	4	73547	3
66364	2	70060	6	73652	1
66550	5	70254	2	73816	4
66650 (*s*)	10	70717 (*s*)	9	74044	2
66742	1	70978 (*s*)	7	74240	3
66862	1	71220 (*s*)	8	74490	1
67030	5	71410	2	74590	1
67163	2	71527	4	74843	1
67266 (*s*)	10	71810	3	74954	1
67460	6	71902	3	75059	1
68060	7	72018	4	75437	0
68235	4	72122 (*s*)	9		
68471	6				

Table II. *Discrete bands of transdichloroethylene (frequencies in wave numbers).*

ν	Intensity	$\bar{\nu}$	Intensity	$\bar{\nu}$	Intensity
65096	6	66891 (*s*)	10	68322	5
65444 (*s*)	10	67111 (a)	3	68486 (b)	1
65813 (*s*)	10	67263 (*s*)	10	68538 (b)	2
66032	1	67466	2	68676	5
66174	7	67621	6	68892	2
66386 (*s*)	9	67835	4	69020	2
66541	7	67954	2	69249	2
66674 (b)	4	68137 (b)	2	69701	1
66752 (b)	5	68188 (b)	3		

(a) This band seemed to be double-headed but the long wave component could not be measured with precision. (b) These bands form pairs appearing as single double-headed bands both heads of which are given in the table.

Table II presents the absorption bands of transdichloroethylene. In this case the frequencies of the violet edges of the bands are given.

Tables III and IV give the diffuse bands for the cis- and transdichloroethylenes, respectively. Since these bands do not possess heads the approximate centers of gravity are given. The 70,080 band of the trans-form is the most intense in the entire spectrum. No intensities are given

Table III. *Diffuse bands of cisdichloroethylene* (frequencies are in wave numbers).

57747, 60562, 61169, 61967, 62605, 78100

Table IV. *Diffuse bands of transdichloroethylene* (frequencies are in wave numbers).

70080, 71000, 74270, 79180, 82000, 83761, 85560, 87010

because they are hard to estimate. The cis-bands with the exception of the last, which is weaker, are about equal in intensity.

$[s]^2$ HCCl A	$[s]^2$ HCCl B	$[y]^2$ HCCl A	$[y]^2$ HCCl B	$[\sigma+\sigma]^2$ C−C
21–24		14–15		13

Below each type of electron is given a rough estimate of the expected ionization potential.

For each molecule three types of symmetry operation in addition to the identity are possible. The application of symmetry properties of polyatomic molecules to their spectra has been discussed by Mulliken[9] and by Herzberg and Teller.[10] It would be beyond the scope of the present article to discuss the selection rules in detail. Suffice to say that if the molecule absorbs either from the nonvibrating level or from a level involving symmetrical vibrations only, in the ground state, a rigid application of the selection rules would permit only symmetrical vibrations to be excited in the upper state.

The two molecules under consideration belong to different symmetry groups, the cis-isomer to group C_{2v} and the trans to group C_{2h}. Using the classification of the various modes of vibration given by Stuart,[11] the following would be totally symmetrical

Transdichloroethylene ν_1, ν_2, ν_4, ν_6, ν_8

Cisdichloroethylene ν_1, ν_2, ν_5, ν_6, ν_9.

Of these frequencies one may be described as C=C stretching, one as C−Cl stretching, one as C−Cl bending, one as C−H stretching and one as C−H bending, although this way of describing the motions is rather qualitative.

For the trans-isomer six frequencies should be active in the infrared and six in the Raman spectrum. Actually more Raman lines have been found,[12] some of which may probably be classified as combination lines. For the cis-isomer all twelve frequencies should be active in the Raman spectrum and ten should be active in the infrared. Ten Raman lines have been observed, some of which cannot be assigned to definite modes of vibration.[12]

III. Discussion of Results

The electron configuration of the transdichloroethylene may be represented as follows[8]

$(3p\pi)^4$ Cl	$(3p\pi)^4$ Cl	$[x+x]^2$ C−C	$(3p\sigma)^2$ Cl	$(3p\sigma)^2$ Cl
nonbonding				
12		11–11.5		

The C=C frequency is 1587 for the cis- and 1577 cm^{-1} for the transdichloroethylene. Carbon-hydrogen stretching frequencies are of the order of 3000 cm^{-1} and carbon-hydrogen bending of the order of 1200 cm^{-1}. The carbon-chlorine frequencies are much lower.[13]

As judged by polarization measurements the lowest frequencies (349 for the trans and 175 for the cis) are symmetrical.[12] The Boltzmann factors for these two frequencies are 0.19 and 0.43, respectively.

It is not possible to classify all of the observed bands unambiguously, although certain regularities are apparent and a qualitative discussion of other important aspects of the spectra is possible.

The continuum observed at the longer wavelengths in both compounds is reminiscent of the continuum found in most compounds containing the carbon-chlorine bond[14] and in all probability this bond is dissociated by absorption in this region of the spectrum. It is reasonable to ascribe the transitions to either the *s* or *y* electrons in the molecule. The diffuse bands on the short wave side of the continuum in the cis-form may indicate that more than one electron state is involved in this region of the spectrum. The frequency differences in these diffuse bands are not very accurate, but one lies in the general region of carbon-hydrogen stretching and the others in the general region of carbon-chlorine stretching, thus indicating that these modes of vibration may be excited without a primary dissociation of the

[8] The authors wish to express their appreciation to Professor R. S. Mulliken for a private communication concerning the electron configurations of these compounds.

[9] R. S. Mulliken, Phys. Rev. **43**, 279 (1933).

[10] G. Herzberg and E. Teller, Zeits. f. physik. Chemie **B21**, 410 (1933).

[11] H. A. Stuart, *Molekülstruktur* (Julius Springer, Berlin, 1934), p. 336.

[12] Cf. B. Trumpy, Zeits. f. Physik **90**, 133 (1934); O. Paulsen, Zeits. f. physik. Chemie **B28**, 133 (1935).

[13] Cf. W. D. Harkins and R. R. Haun, J. Am. Chem. Soc. **54**, 3920 (1932).

[14] G. Herzberg and G. Scheibe, Zeits. f. physik. Chemie **B7**, 390 (1930).

TABLE V. *Rydberg series in cisdichloroethylene.*

A. $\bar{\nu}=77703-R/(m-0.045)^2$			$m=3, 4, 5, 6, \cdots$	
Obs.	65164	70717	73205	74590
Calc.	65136	70688	73233	74609
Diff.	−28	−29	+28	+19
B. $\bar{\nu}=78103-R/(m-0.01)^2$			$m=3, 4, 5, 6, \cdots$	
Obs.	65845	71220	73652	75059
Calc.	65829	71210	73696	75045
Diff.	−16	−10	+44	−14

molecule. The appearance of the bands is, however, strongly suggestive of predissociation.

The discrete bands, at least in the cis- and probably also in the trans-form, seem to belong to several different upper electron states. This is indicated by the fact that two different Rydberg series are found among the bands of the cisdichloroethylene. Table V shows the agreement between observed and calculated frequencies for the two series.

The convergence limits of these two series both lie in the short wave region of continuous absorption. The predicted ionization potentials are 9.58 and 9.63 volts, both of which lie well below the ionization potentials estimated by Mulliken[8] for the transdichloroethylene. The fact that the two chlorine atoms are on the same side of the molecule, thus leading to a dipole moment considerably higher than for the trans-form would lead one to expect such an effect on the ionization potential.

Actual measurement of the ionization potential by the method previously described[7] gave a value of 9.7 ± 0.3 electron volts, which is well within experimental error of the value predicted spectroscopically.

No Rydberg series could be found among the bands of transdichloroethylene, but an experimental determination of the ionization potential by the method of electron bombardment gave a value of 11.3 volts, which agrees reasonably well with the ionization potential predicted by Mulliken[8] for the x electrons of the C=C bond.

The classification of the remaining bands of the cis-form among vibration levels is not possible without introducing arbitrary frequencies in such a manner that the meaning would be doubtful. Table VI shows some differences based on the bands in the B series of Table V.

Differences based on the A system of Table V are not as consistent as those for the B system,

TABLE VI. *Tentative progressions in the bands of cisdichloroethylene.*

65845	71220	65845	70060 (185)	69875
1421	1420	175	194	
67266	72640	66020	70254	
1404	1404			
68670	74044	67266		
1390	1393	194		
70060	75437	67460		
1350				
71410		68670 (199)	68471	
		202		
		68872		
			71220	74044
			190	196
			71410	74240

although in each case frequencies between 1400 and 1500 and near 200 may be found.

There seems little doubt that the frequency about 1420 cm^{-1} is a modification of the C=C frequency which is 1587 cm^{-1} in the ground state. The frequency near 200 must be a modification of the deformation frequency 175 in the ground state. There seems to be little point in attempting a further classification of these bands, since it would be necessary to introduce too many arbitrary frequency differences. The electronic excitation in these bands is almost certainly connected with the C=C bonding electrons, either σ or x. Since the electric moment may change along any one of the three axes, there should be three upper electron states for a given electronic transition. Actually only two Rydberg series were found, although some evidence was found for a third. It seems impossible to state at present just what changes in vibration frequencies would be expected from one substate to another and this is one reason why a complete systematic classification of the bands is impossible.

The bands of transdichloroethylene may be classified into a vibrational scheme using one quantum number in the ground state and two in the upper. Here as in the cis-form it seems necessary to assume that the lowest deformation frequency is almost the same in the lower state as in the upper state. This makes unambiguous classification of the bands difficult, but intensity relationships furnish support for the tentative scheme given in Table VII.

The remaining bands of Table II are subheads of the double headed bands. While the significance is not clear it is noted that these double-headed bands all occur together in the B system

TABLE VII. *Tentative classification of the bands of transdichloroethylene.*

		A SYSTEM			
65444	(348)	65096	65444	66891	68322
1447		1445	369	372	354
66891	(350)	66541	65813	67263	68676
1431		1413	361	358	344
68322	(368)	(67954)	66174	67621	69020
1382					
69701					
		B SYSTEM			
66386	(354)	66032	66386	67835	
1449		1434	366	353	
67835	(369)	67466	66752	(68188)	
1414		1426	359	350	
69249	(357)	68892	67111	68538	

when both frequencies are involved in the upper state

The connection between the A and B systems is not obvious. It is true that by introducing one more mode of vibration a connection could be found, but it seems more probable that different electron states are involved. In the trans-form change of dipole moment will lead to only two different configurations since two will be identical. It is possible that such sub-electron states are involved, but a complete answer to the question here raised must await further theoretical developments.

The continuous absorption observed in both forms deserves some consideration. The most intense absorption in the trans-form is first noticeable at 70,080 cm^{-1} at low pressures and broadens approximately symmetrically with increasing pressure until the entire discrete absorption is obliterated by the continuum. There is a minor region of absorption at a frequency about 900 cm^{-1} higher. It may be worthy of note that there is a symmetrical frequency at 847 cm^{-1} observed in the Raman spectrum.[12] There is still a further region of continuous absorption beginning at 74,270, or a little over 3000 cm^{-1}, higher than the previous band. These regions of absorption have some of the characteristics of predissociation bands. The one at 70,080 corresponds to about 200,000 calories per mole which, is some 50,000 calories more than that necessary to dissociate the carbon-carbon double bond. It seems probable that this bond is dissociated in this continuum, the excess energy appearing either as excitation energy or kinetic energy or both.

The difference between the continuum at 70,080 and the next higher region is very closely the same as the difference between the frequencies of the bands tentatively taken as 0,0 bands for the A and B systems. Moreover the main progressions in both systems involve the carbon-carbon frequency, so that perturbation between the upper vibration levels of this state and the next higher electron state may be responsible for the predissociation.

In the cisdichloroethylene there are no regions of continuous absorption corresponding to those just mentioned for the trans-form. Continuous absorption starts about 78,100 cm^{-1} and broadens, particularly toward shorter wavelengths, as the pressure is increased. This continuum is weaker than those in the transdichloroethylene and falls just about at the convergence limit of the two Rydberg series.

Price[15] has found a Rydberg series in ethylene predicting an ionization potential of 10.41 volts but makes no mention of a continuum at a corresponding frequency. He does mention that numerous faint bands were observed which were not classified. It is possible that the abundance of bands near the convergence limits of the two Rydberg series in the cis-form is partially responsible for the continuous appearance of the absorption. In general one would not expect to find a continuum corresponding to the removal of one electron from a complex molecule of this type. It seems more probable that the continuum is due to a transition to an upper electron state which is repulsive. Just what dissociation is involved may only be conjectured, although it is probably that of the carbon-carbon bond. The energy is, however, some 70,000 calories per mole more than that necessary to produce such a dissociation. There is the further possibility that simultaneous removal of two chlorine atoms may occur.

The continuum which starts at 68,000 cm^{-1} in the region of discrete absorption may involve a weak transition to a repulsive upper state producing dissociation of the carbon-carbon bond.

In conclusion the authors wish to express their appreciation to Dr. A. B. F. Duncan for help during the experimental work and to Dr. E. B. Wilson, Jr. of Harvard for a conversation concerning the symmetry properties of the two molecules under discussion.

[15] W. C. Price, Phys. Rev. **47**, 444 (1935).

The Absorption Spectrum of Diacetylene in the Near Ultraviolet

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The absorption spectrum of diacetylene gas was investigated down to λ1900A. In the region λλ2860–1900A more than eighty bands were found. Some regularities in the spectrum and the similarity with the cyanogen ultraviolet absorption spectrum are described. Resemblance between the diacetylene and cyanogen molecules is briefly discussed.

A GREAT deal of interesting and useful results regarding the structure of diatomic molecules in the normal as well as in the excited states have been obtained from their spectroscopic investigations. For polyatomic gases, however, on account of their increasing complexity, only in few of the simplest cases have their spectra and structure been completely understood. Very interesting results regarding the structure of simple polyatomic molecules in the excited states could, however, be obtained through an investigation of their ultraviolet absorption spectra in cases where the structure in the normal states has been definitely established. Some three years ago, the ultraviolet absorption spectrum of cyanogen was studied by Badger and one of the present authors.[1] It was found that the spectrum is extremely complex, and no complete analysis could be made. A comparison of the diacetylene molecule with that of cyanogen would immediately suggest that these molecules are isosteric and probably have similar electronic states. This has actually been proved to be the case in the normal state.[2] It seems to be probable that a study on the ultraviolet absorption spectrum of diacetylene may throw some light on the structure of both of these molecules in the excited states.

EXPERIMENTAL PROCEDURE

The diacetylene gas used in the investigation was prepared by the method of Straus and Kollek.[3] The gas generated was condensed in a solid CO_2 trap when thoroughly washed and dried. It was purified by repeated fractionation under vacuum, until the first, middle and last portions showed no difference in the spectrum.

A glass tube of about 130 cm long, fitted with fused quartz windows and connections to trap, manometer and vacuum pump, was used as the absorption cell. The spectrum was taken with a Hilger E 31 quartz spectrograph. A hydrogen discharge tube of the type described by Sheibe[4] was used as the continuous light source. The authors want to express their sincere thanks to Dr. Herzberg through whose kindness the discharge tube was obtained. The tube was excited with a power of about 1 kva through a 9000 v transformer. Eastman 40 plates sensitized with light oil were used. As comparison spectrum copper spark lines were employed. Exposure of one hour was found sufficient.

After the introduction of freshly distilled diacetylene in the liquid air trap, the system was thoroughly evacuated with an oil pump to get rid of any volatile impurities which might be present during the preparation. The pressure of the absorbing gas varied from 1 mm to 252 mm. It was found that the development of the bands was very critical to pressure. Plates were thus taken at adjusted pressure intervals in order to develop the system as completely as possible, and for each pressure two or three plates were taken.

During the exposure, slight polymerization of the gas was observed, but it had no influence on the nature of the spectrum.

Measurement of the bands were made with a S. I. P. Comparator* for 16 plates, each being measured three to six times. On account of the

[1] Sho-Chow Woo and Richard M. Badger, Phys. Rev. **39**, 932 (1932).
[2] B. Timm and R. Mecke, Zeits. f. Physik **94**, 1 (1935).
[3] F. Strauss and L. Kollek, Ber. d. Deutsch. chem. Ges. **59**, 1664 (1926).
[4] G. Scheibe, F. Povenz and C. F. Linström, Zeits. f. physik. Chemie **B20**, 283 (1933).

* Our thanks are due to Professor S. L. Ting and Dr. Z. W. Ku for the privilege of using the instrument of the Physics Institute.

great pressure broadening on part of the bands, great accuracy may not be expected. Great difficulty was also experienced in deciding exactly what part of a band to measure, for the appearance of the bands varies considerably from band to band. But in the case of sharp bands the error may not be greater than 10 cm^{-1}.

Results and Discussion

At 1 mm pressure (130 cm absorption length), diacetylene was found to be completely transparent to λ2490A, where a group of strong bands set in and extended to the short wavelength limit of the spectrograph. Some of the strong bands are degraded to the red, while most of them do not show any sharp edge. With increasing pressure, the bands became broadened and appeared finally as an apparent continuum, which shifted gradually toward the red side, till at a pressure of about 10 mm, all of the low pressure bands were completely obliterated and another group of bands began to appear. This last group of bands extended toward the red side with increasing pressure, until at 252 mm it extended as far as λ2860A.

Because of the varying appearance of the bands, it is rather difficult to determine how best to describe their general nature, until our more detailed investigation with higher dispersion is finished. It may, however, be said that the low pressure group of bands shows somewhat different gross structure from that of the higher pressure group. Table I gives the wavelengths and wave numbers of the bands measured, their relative intensities being estimated visually.

The fundamental frequencies of diacetylene in the normal state have been discussed by Mecke.[2] The valence vibrational frequencies may not be expected to appear as differences in the ultraviolet absorption spectrum at room temperature. On the other hand, weaker bands should appear on the red side of the strong bands at distances equal to the deformation vibrational frequencies from the latter. It is rather curious why these bands should be absent in the spectrum.

Six progressions of reasonable intensity distribution are given in Table II. It will be noticed that all of them have a frequency difference of about 2100 cm^{-1}. Other similar progressions could have been assigned by including the higher pressure bands. But the peculiar intensity distribution make them uncertain. Without considering the coupling effect between different vibrations which causes its variation from one progression to another, the frequency difference

Table I. *The diacetylene bands in the near ultraviolet.*

M	λ(*A*)	ν(cm⁻¹)	*I*	*M*	λ(*A*)	ν(cm⁻¹)	*I*	*D*
	2861.4	34938	00		2498.9	40006	0	
	2851.5	35059	00		2485.3	40224	3	
	2808.4	35597	00		2476.5	40367	1	
	2805.2	35638	0	VE	2467.3	40518	4	
	2802.1	35677	00		2460.3	40633	0	
	2798.3	35725	00		2450.2	40801	0	
	2793.2	35791	00		2446.3	40866	0	
	2787.6	35863	00	VE	2429.5	41148	10	*A*
	2782.3	35931	00		2422.0	41276	5	*B*
	2777.6	35992	00		2407.7	41521	5	*C*
D	2755.0(?)	36287	3		2403.5	41593	5	*D*
D	2751.3(?)	36336	2	VE	2393.0	41776	6	*E*
D	2746.3(?)	36402	3		2388.7	41851	0	
D	2738.4	36507	0		2384.6	41923	0	
D	2732.0	36592	0		2380.3	41999	0	
D	2724.2	36697	0		2375.7	42080	3	*F*
D	2716.8	36797	0		2364.4	42281	1	
VE, (D)	2698.8	37043	4		2359.3	42372	2	
	2694.0	37109	3		2351.9	42506	1	
	2688.5	37184	0		2346.7	42600	3	
	2683.6	37252	0	VE	2310.8	43262	9	*A′*
D	2677.9	37332	1		2303.0	43408	4	*B′*
D	2670.2	37439	3		2292.6	43605	4	*C′*
	2664.5	37519	2		2287.9	43695	4	*D′*
	2657.5	37618	0	VE, (D)	2281.8	43811	5	*E′*
	2652.6	37688	2		2276.3	43917	2	
D	2648.8	37742	4		2263.2	44172	3	*F′*
	2641.9	37840	1		2254.9	44334	1	
	2637.7	37901	2		2246.8	44494	1	
D	2630.5	38004	1		2236.9	44691	3	
	2623.5	38106	0	VE	2204.2	45354	5	*A″*
D	2617.3	38196	3		2196.5	45513	2	*B″*
	2606.9	38348	2		2189.3	45662	2	*C″*
	2599.1	38463	1		2179.3	45872	2	*E″*
	2592.9	38555	0		2161.4	46252	2	*F″*
	2586.8	38646	0		2117.9	47202	1	
VE, (D)	2553.4(?)	39152	2	VE	2108.2	47419	3	*A‴*
	2513.6	39772	0		2100.8	47586	1	*B‴*
	2506.3	39887	0		2085.3	47939	1	*E‴*

In columns *M*, VE indicates the violet edge of the bands measured, for other bands not specified centers of them being measured. D means diffused.

Columns *I* and *D* give respectively the estimated relative intensities and designations.

Table II. *Some progressions in the diacetylene spectrum.*

ν (cm⁻¹)	Δν	ν (cm⁻¹)	Δν	ν (cm⁻¹)	Δν
A		*B*		*C*	
A 41148	2114	*B* 41276	2132	*C* 41521	2084
A′ 43262	2092	*B′* 43408	2105	*C′* 43605	2057
A″ 45354	2065	*B″* 45513	2073	*C″* 45662	
A‴ 47419		*B‴* 47586			
D		*E*		*F*	
D 41593	2102	*E* 41776	2035	*F* 42080	2092
D′ 43695		*E′* 43811	2061	*F′* 44172	2080
		E″ 45872	2067	*F″* 46252	
		E‴ 47939			

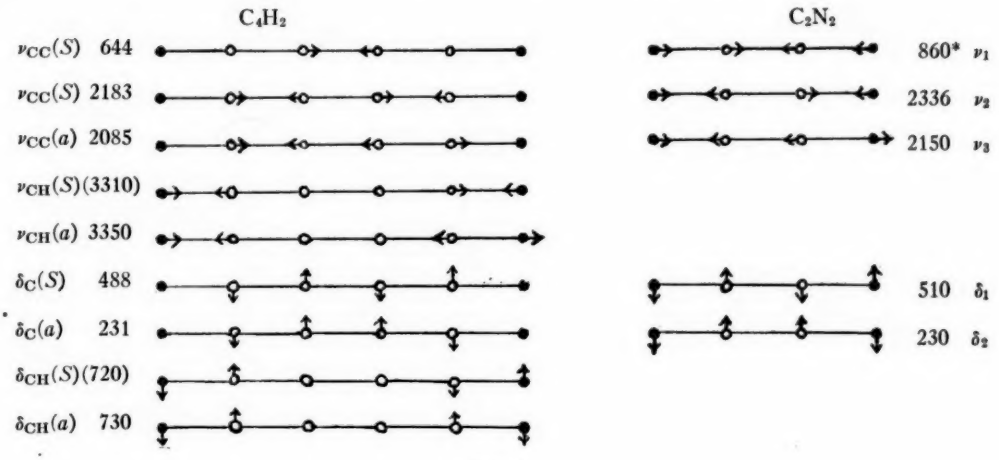

FIG. 1.

$\sim$2100 cm^{-1} is considered to be approximately the frequency of a longitudinal vibration in the excited state.

The similarity between the structure of diacetylene and cyanogen in the normal state has been pointed out by Mecke through an investigation of their infrared and Raman spectra. The normal vibration frequencies are given in Fig. 1. Because these compounds contain the same number of electrons, it may be inferred that they should possess similar electronic states. An examination of their ultraviolet absorption spectra shows fairly definitely that these systems are due to transitions between corresponding electronic states, the lower states being the normal. First of all, these spectra appear almost in the same region. The spectrum of diacetylene as in the case of cyanogen will certainly extend farther into the vacuum region than what we have reported here. Secondly, the gross structure of these spectra shows marked similarities. Thus in both of them the strongest and longest progressions have a frequency difference of $\sim$2100 cm^{-1}, which represents a normal vibrational frequency in the excited states probably having similar symmetrical character in both cases. Before the complete analysis of the spectra is obtained, one may not be able to ascertain the exact structure of these molecules in the excited state and the selection rules governing the transitions in the ultraviolet spectra. But it may be pointed out that the probability of transitions is influenced by two factors. Firstly the symmetry of the molecule determines the selection rule. Secondly transitions which may be allowed by the symmetry characters may still be excluded for reasons which are analogous to those leading to the Franck-Condon principle for diatomic molecules. If the vibration 2100 cm^{-1} in the excited states is taken to be of similar symmetry character for the two molecules, a reference with the vibration diagram given above will show that the excited electronic states of diacetylene and cyanogen molecules are similar in symmetry character, and that the internuclear distances in the excited states with those in the normal states have the same kind of relation in both cases.

The above argument does not necessarily mean that the structures of the diacetylene and cyanogen molecules should not differ from each other in details. For example, one of the molecules may be slightly bent, while the other is collinear. This may not affect some of the vibrational frequencies very much, but will certainly modify the selection rules considerably. This effect has already been observed in the infrared and Raman spectra of diacetylene.

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* According to our recent calculation (to appear in the J. Chinese Chem. Soc.) there may still be some doubt about the value 860 cm^{-1} assigned to the longitudinal vibration ν_1, which seems to be 756 cm^{-1} as observed in Raman spectrum (A. Petrikaln und J. Hochberg, Zeits. f. physik. Chemie **B8**, 440 (1930)).

The Absorption Spectra and Dissociation Energies of Cyanic Acid and Some Isocyanates

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The absorption spectra of gaseous isocyanic acid, methyl, ethyl and phenyl isocyanates have been observed in the ultraviolet. The long wavelength limits of the continuous absorption found were as follows: HNCO, λ2240; CH_3NCO, λ2550; C_2H_5NCO, λ2480; C_6H_5NCO, λ2420A. In the case of isocyanic acid, diffuse bands were also found in the region λλ2570–2250A. Characteristic absorption bands due to an excitation in the benzene ring were found in phenyl isocyanate. The structures are probably represented by the formulae $H-N=C=O$, $CH_3-N=C=O$, $C_2H_5-N=C=O$, $C_6H_5-N=C=O$. The products and energies of dissociation have been described. The absence of the characteristic absorption due to $>C=O$ has also been discussed.

THE structure of cyanides and cyanates has long been a subject of numerous investigations. Most of the classical studies were, however, limited to solutions. Recently a great deal of interesting results have been obtained through spectroscopic investigations on simple cyanides. Quite lately, the Raman spectra of isocyanates have been investigated by Kohlrausch and others.[1] It seemed probable that a study of the ultraviolet absorption spectra might yield some interesting information regarding the nature and strength of binding and the structure in some organic cyanates.

EXPERIMENTAL

The chemicals employed for preparation of the substances used in this investigation were of c. p. grade, unless otherwise stated.

Cyanic acid was prepared by heating cyanuric acid (Technical, Eastman Kodak Co.). The gas obtained was condensed in a trap cooled by freezing mixture. On account of the rapid polymerization of liquid cyanic acid, purification was effected by distillation under vacuum between freezing mixture and liquid air temperatures. The middle portions only were taken for the experiment. Under such conditions, no appreciable polymerization was observed and the product thus obtained was a colorless liquid.

Methyl isocyanate was prepared according to Slotta and Lorenz[2] by heating a mixture of freshly distilled dimethyl sulfate (Kahlbaum, "for scientific purpose") and potassium cyanate in the presence of anhydrous sodium carbonate. The product was purified by repeated distillations and finally the portion of B. P. 42–42.5°C was collected. As shown by the spectrum, traces of sulfur dioxide (<0.5%) probably from the decomposition of the sulfate were found present. Since the spectrum of sulfur dioxide is well known and no convenient method is available for its separation when present in such a small quantity, no further purification was applied.

Ethyl isocyanate was prepared by the same method as for methyl isocyanate, Kahlbaum technical dimethyl sulfate being used in this case. After repeated distillations, the middle portion of B. P. 60°C was collected for use. Traces of sulfur dioxide were also found present.

Phenyl isocyanate used was a Kahlbaum scientific preparation. Preliminary experiments showed that the freshly redistilled product gave the same spectrum as the original material, which was then used without further purification.

The spectra were taken with a small Hilger quartz spectrograph, a hydrogen discharge tube being used as the continuous light source. The time of exposure was generally one hour. Absorption cells of 10 cm, 130 cm and 285 cm length were employed. The pressure of phenyl isocyanate was its vapor pressure at room temperature, while those of methyl and ethyl isocyanate varied from 1 mm up to 274 mm and 131 mm, respectively. On account of the violent polymerization of the liquid above 0°C, the highest pressure of cyanic acid used was its vapor pressure at this temperature. One experiment was carried out with a pressure of 373 mm by leading the gas generated from the decomposition of

[1] K. W. F. Kohlrausch, *Der Smekal-Raman Effekt* (1931), pp. 246–247, 321, 332.

[2] K. H. Slotta and L. Lorenz, Ber. D. Chem. Ges. **58**, 1320 (1925).

cyanuric acid directly into the absorption cell. No difference in the spectrum was observed. But polymerization was considerable. Experiments with different amounts of the absorbing gas were considered necessary for the following reasons. In the case of continuous absorption, bands may sometimes be found at low pressures, if the continuum at moderate pressures is only apparent; while with increasing pressure the continuous absorption may be displaced toward the red side so that the upper limit of dissociation energy may be estimated more nearly to the true value. In the case of discrete absorption, the system of bands may be more completely developed with varying amounts of the absorbing gas. Actually this was found true here as is usually the case.

Results and Discussion

In the cases of methyl and ethyl isocyanates only continuous absorption was found, and a careful search failed to detect any discrete bands.* For phenyl isocyanate, bands corresponding to the characteristic absorption of the phenyl group were found in the region λλ2770–2550A in addition to the continuum. The long wavelength limits of the continuous absorption of methyl and ethyl isocyanates were found to shift toward greater wavelength with increasing amounts of the absorbing gas, finally approaching a value which remained almost constant with further increase of the absorbing gas. In the case of cyanic acid, very diffuse bands immediately followed by a continuum appeared in the region λλ2570–2250A. With varying amounts of the absorbing gas, the extension of the band system and the long wavelength limit varied considerably. These bands were so diffuse and broad that only their approximate wavelengths could be given. Moreover, because of the low dispersion used, it was not possible to determine which of the bands are really without fine structure. The long wavelength limit of the continuum in this case was estimated when the amount of the absorbing gas was at such an optimum value that the bands of shortest wavelength just began to appear. The results of the measurements are presented in Table I.

* A group of faint bands was found in the region λλ3100–2500 at highest pressure of the absorbing gases (130 cm absorption length). This was finally proved to be due to sulfur dioxide.

Table I.

Molecules	Continua λ(A)	Energies of dissociation (Kcal./mole)
HNCO	>2240	<126.9
CH_3NCO	>2550	<111.5
C_2H_5NCO	>2480	<112.4
C_6H_5NCO*	>2420	<117.5

Approximate wavelength of HNCO bands:
2565, 2545, 2528, 2513, 2505, 2495, 2477, 2465, 2445, 2434, 2415, 2400, 2385, 2370, 2357, 2345.

* Bands due to phenyl group are not given.

As a result of the light absorption, the molecules are either excited when discrete absorption appears or directly decompose where a continuum results. The absorption bands of phenyl isocyanate are certainly due to an electronic excitation in the benzene ring for they are similar to the phenyl bands of aniline with respect both to the spectral region, the band spacings and the intensity distribution. The discrete absorption of cyanic acid appears in about the same region as in the cases of primary, secondary and tertiary amines.[3] They are thus probably due to an electronic excitation of the $H-N\langle$ bond. The differences in band spacings and intensity distribution in these two cases may be what we should expect for the asymmetry of the cyanic acid molecule ($H-N=C=O$) in comparison with the molecules of the amines. Thus the structure of gaseous cyanic acid may be represented by $H\text{--}N=C=O$. A comparison of the spectral regions where the continua set in will show that the methyl, ethyl and phenyl compounds have probably a similar structure $R-N=C=O$.

The results obtained by Kohlrausch and others[1] from Raman spectrum investigations also indicate the structure $R-N=C=O$ for the molecules of methyl, ethyl and phenyl isocyanates† in the liquid state.

It will be seen that in all these cases there was found no absorption characteristic of the carbonyl group $\rangle C=O$, which has been observed for aldehydes and ketones. The characteristic ab-

[3] G. Herzberg and R. Kölsch, Zeits. f. Elektrochemie **39**, 572 (1933).

† New results on the Raman spectra of methyl and ethyl isocyanates have been obtained by H. Kopper and A. Pongratz (Monatsh. **62**, 78–89 (1933)). Unfortunately this original paper is not available here.

sorption of $>C=O$ may, however, be influenced to a certain extent by the nature of the group or groups attached to the carbon atom. Thus in the case of aldehydes and ketones, this absorption appears, generally in the region λλ3400–2500A, while in the case of carboxylic acids and esters, it is displaced considerably to the shorter wavelength.[4] It will be further noticed that isocyanic acid HNCO is isosteric with carbon dioxide and ketene and all of them contain the $>C=O$ group. The absorption bands of ketene set in at 3850A[5] while no absorption of carbon dioxide has been observed until 1850A.[6] Hence the absence of absorption ~3000A in the case of the isocyanates may not be an evidence for the absence of $>C=O$ group in these molecules. Recently Herzberg[3] has also failed to find the absorption characteristic of $>C=O$ and NH in gaseous formamide and seemed to incline to the revision of the classical formula $H-C(=O)-H_2N$. On the other hand, the existence of the carbonyl group as well as the amino group seems to have been definitely proved in the liquid formamide by Raman spectrum investigations.[7] It will be interesting in this connection to investigate the absorption spectrum of liquid formamide.

In each of these cases the long wavelength limit of the continuum is taken as the upper limit of the dissociation energy of the molecule. In the case of cyanic acid, predissociation might have started at longer wavelength and thus the value given here is probably somewhat too high. If a structure of the isoform $R-N=C=O$ is assumed for each of these molecules, photochemical dissociation may take place at one of the three bonds, $R-N$ ($H-N$, $C_{al}-N$, $C_{ar}-N$), $N=C$ and $C=O$. The bond energy of $N=C$ amounts to about 125 Kcal.,[8] while that of $C=O$ about 180 Kcal. The bond energies for $H-N$ and $C-N$ may be taken approximately as 87 Kcal. and 60 Kcal., respectively. It will be seen that the optical dissociation energies are only sufficient to account for the splitting of the $R-N$ bonds. The excess of energy for each case is as follows: $H-NCO$ 39.9 Kcal., CH_3-NCO 51.5 Kcal., C_2H_5-NCO 52.4 Kcal., and C_6H_5-NCO 57.5 Kcal. Unfortunately neither is any thermochemical datum available nor are the energies of activation for NCO, CH_3, C_2C_5 and C_6H_5 definitely known for a direct comparison.

[4] See, e.g., J. Bielecki and V. Henri, Ber. D. Chem. Ges. **46**, 3627 (1913); G. Scheibe, F. Povenz and C. F. Linström, Zeits. f. physik. Chemie **B20**, 283 (1933).

[5] G. C. Lardy, J. Chim. Phys. **21**, 353 (1924); R. G. W. Norrish, H. G. Crone and O. Saltmarsh, J. Chem. Soc. 1533 (1933).

[6] Leifson, Astrophys. J. **63**, 82 (1926); Lyman, *Ultraviolet-spektroscopie*.

[7] K. W. F. Kohlrausch, reference 1, p. 313.

[8] N. V. Sidgwick, *The Covalent Link in Chemistry* (1933), p. 119.

Errata: Experimental Investigation of the Effect of Pressure on Phase Equilibria of Sodium Tungstate and of Related Thermodynamic Properties

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(J. Chem. Phys. **3**, 87, 1935)

IN Table 4, column 3, on page 91, read dt/dp instead of dp/dt.

The first equation in the second column on page 92 should be

$$v-v_{20}=v_{20}[53.194(t-20)10^{-6}+41.5(t-20)^2 10^{-9}]$$

instead of

$$v-v_{20}=v_{20}[53.194(t-20)10^{-6}+41.5(t-20)^2 10^{-8}].$$

The Normal State of the Helium Molecule Ion, He_2^+

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A variation function constructed of hydrogen-like 1*s* functions with different values of the effective nuclear charges for He: and He.$^+$ is used in the treatment of the normal state of the helium molecule-ion. The treatment leads to the values $D_e=2.22$ e.v. and $r_e=1.097$A for the dissociation energy and the internuclear distance, in good agreement with the experimental values.

THE normal state of the helium molecule-ion, He_2^+, was treated by Pauling[1] who used a simple wave function constructed of hydrogen-like 1*s* functions $\psi=Z^{3/2}\pi^{1/2}e^{-\xi/2}$ with $\xi=2Zr_A$ and a similar expression in r_B for φ. The energy expression was minimized with respect to the effective nuclear charge Z and good agreement with the experimental values was obtained. In this treatment the same effective nuclear charges were assumed for the helium atom and the helium ion, the same function being used in calculating energies at small distances and at infinity. Though this does not provide a very good approximation at infinity we might expect the errors to be about the same as at $r=r_e$ and as a matter of fact the dissociation energy, being the difference of the energy values at infinity and at r_e, came out in a very good agreement with the experimental value.

It should be expected that a much closer approximation to the wave function would result from the use of different effective nuclear charges for the helium atom and the helium ion, in which case we would have at infinity a correct wave function for He^+ and a reasonably good approximation (the screening-constant type) for He, and we might consider the approximation at $r=r_e$ to be quite good also. In any case the repetition of the calculation with different effective nuclear charges for the atom and for the ion will provide us with some basis of judgment as to the reliability of such a treatment.

For this purpose two antisymmetric functions ψ_{I} and ψ_{II} can be constructed by Slater's method which would be represented by the following scheme:

	ψ	φ	ξ	η
I	$\pm$			+
II		$\pm$	+	

[1] Linus Pauling, J. Chem. Phys. **1**, 56 (1933).

where ψ and φ refer to the helium atom and ξ and η to the helium ion, with the effective nuclear charges Z for the atom and $Z'=\epsilon Z$ for the ion, ϵ thus representing the ratio of the effective nuclear charge of the ion to that of the atom.

The wave equation for a hydrogen-like atom, in a system of units with unit of length $a_0=0.52845$A, unit of charge e and unit of energy $e^2/a_0=27.06$ volt electrons, is

$$\nabla^2\psi+2(W-V)\psi=0, \tag{1}$$

which can be rewritten as

$$-\tfrac{1}{2}\nabla^2\psi+V\psi=W\psi, \tag{1a}$$

where $W=-Z^2/2$. The general wave equation may be written as

$$H\psi=W\psi, \tag{2}$$

with

$$H=-\tfrac{1}{2}\nabla^2+V \quad \text{and} \quad V=\Sigma\Sigma(Z_iZ_j/r_{ij}), \tag{3}$$

the Hamiltonian function for the case of the helium molecule-ion being

$$H=-\tfrac{1}{2}(\nabla_1^2+\nabla_2^2+\nabla_3^2)-2/r_{A1}-2/r_{A2}-2/r_{A3}-2/r_{B1}-2/r_{B2}-2/r_{B3}+1/r_{12}+1/r_{13}+1/r_{23}+4/r_{AB}. \tag{4}$$

The variational integral

$$E=\int\psi^*H\psi d\tau/\int\psi^*\psi d\tau$$

for our wave function takes the form

$$E=\int H(\psi_{\text{I}}-\psi_{\text{II}})^2d\tau/\int(\psi_{\text{I}}-\psi_{\text{II}})^2d\tau=H_{\text{I I}}-H_{\text{I II}}/d_{\text{I I}}-d_{\text{I II}} \tag{5}$$

where

$$H_{\text{I I}}=(\psi_1\psi_2\eta_3|H|\psi_1\psi_2\eta_3)-(\psi_1\psi_2\eta_3|H|\eta_1\psi_2\psi_3) \tag{6}$$

and

$$H_{I\,II}=(\psi_1\psi_2\eta_3|H|\varphi_1\varphi_2\xi_3)-(\psi_1\psi_2\eta_3|H|\xi_1\varphi_2\varphi_3). \quad (6a)$$

The different integrals occurring in subsequent calculations will be indicated by letters I or F ($I=ZF$) with subscripts. Letters s and t will be used for integrals of the type $\int\psi\varphi d\tau$. A table of all integrals used will be found in the appendix.

Leaving out for the present the term $4/r_{AB}$ in the Hamiltonian we can set up the following expressions:

$$\begin{aligned}
&\int\xi_1H_1\xi_1d\tau_1=\epsilon^2Z^2/2-2\epsilon Z(1+F_{1\epsilon})=A\\
&\int\xi_1H_1\eta_1d\tau_1=\epsilon^2Z^2(F_{2\epsilon}-s_\epsilon/2)-4\epsilon ZF_{2\epsilon}=B\\
&\int\psi_1H_1\psi_1d\tau_1=Z^2/2-2Z(1+F_1)=C\\
&\int\psi_1H_1\varphi_1d\tau_1=Z^2(F_2-s/2)-4ZF_2=D\\
&\int\psi_1H_1\xi_1d\tau_1=-\epsilon^2Z^2t_0/2+\epsilon Z^2F_7\\
&\qquad\qquad -2Z(F_7+F_8)=E\\
&\int\xi_1H_1\psi_1d\tau_1=-Z^2t_0/2+Z^2F_7\\
&\qquad\qquad -2Z(F_7+F_8)=E'\\
&\int\varphi_1H_1\xi_1d\tau_1=-\epsilon^2Z^2t_0/2+\epsilon Z^2F_9\\
&\qquad\qquad -2Z(F_9+F_{10})=K\\
&\int\xi_1H_1\varphi_1d\tau_1=-Z^2t/2+Z^2F_{10}\\
&\qquad\qquad -2Z(F_9+F_{10})=K'.
\end{aligned} \quad (7)$$

Then, in terms of A and B, we have

$$\begin{aligned}
H_{I\,I}&=A+(2-t^2)C-t(K+K')+\tfrac{5}{8}Z\\
&\qquad +2ZF_{11}-2ZtF_{12}+ZF_{13}\\
H_{I\,II}&=s^2B+(2ss_\epsilon-t_0^2)D-st_0(E+E')+Zs_\epsilon F_6\\
&\qquad +2ZsF_{14}-2Zt_0F_{15}-ZsF_{16}\\
d_{I\,I}&=1-t^2\\
d_{I\,II}&=s^2s_\epsilon-st_0^2.
\end{aligned} \quad (8)$$

Now we can write the energy integral, including the term $4/r_{AB}$, as

$$E=\frac{4}{r_{AB}}+\frac{H_{I\,I}-H_{I\,II}}{d_{I\,I}-d_{I\,II}}=\frac{4Z}{\rho}+\frac{2Z^2+\mu Z}{\nu} \quad (9)$$

where

$$\begin{aligned}
\lambda&=1+\epsilon^2/2+\epsilon^2t^2/2+s^2s_\epsilon(1+\epsilon^2/2)\\
&\quad -(st_0^2/2)(\epsilon^2+2)-(2ss_\epsilon-t_0^2)F_2-\epsilon^2s^2F_{2\epsilon}\\
&\quad +(\epsilon+1)st_0F_7-t(\epsilon F_9+F_{10})
\end{aligned} \quad (10)$$

$$\begin{aligned}
\mu&=-27/8+2(t^2-\epsilon)-2(2-t^2)F_1-2\epsilon F_{1\epsilon}\\
&\quad +4(2ss_\epsilon-t_0^2)F_2+4\epsilon s^2F_{2\epsilon}-s_\epsilon F_6+\\
&\quad -4st_0(F_7+F_8)+4t(F_9+F_{10})+2F_{11}\\
&\qquad -2tF_{12}-F_{13}-2sF_{14}+2t_0F_{15}+sF_{16}
\end{aligned} \quad (10a)$$

and

$$\nu=1-t^2-s^2s_\epsilon+st_0^2. \quad (10b)$$

Minimizing (9) with respect to Z we obtain

$$Z_{\min}=-(\nu/2\lambda)(4/\rho+\mu/\nu), \quad (11)$$

and substituting this value of Z in (9) we have

$$E_{Z=\min}=-(\nu/4\lambda)(4/\rho+\mu/\nu)^2. \quad (12)$$

Expression (12) is a function of ρ and ϵ and the best set of values of ρ and ϵ, corresponding to a minimum for E, was obtained by direct substitution of different values. The procedure employed was as follows: first for a given value of ρ the best value of ϵ was obtained; then ρ was varied to get the best value of ρ for the value of ϵ obtained in the previous step; then ϵ was varied again, and so on, until the variation of neither ϵ or ρ would result in a lower value of E. However, as the numerical calculations involved are very laborious and the variations in energy very small, ρ was calculated only to two significant figures and ϵ to three. The values obtained are $\rho=3.6$, $\epsilon=1.17$ and $E=4.930$, with $Z=1.734$ and $Z'=2.029$ at the equilibrium distance. At $r=\infty$ the corresponding values are $\epsilon=32/27=1.185$ and $E=4.848$, with $Z=27/16=1.6875$ and $Z'=2.000$. This gives for the dissociation energy the value $D_e=2.22$ e.v. and for the internuclear distance $r_e=1.097$A, in very good agreement with the experimental values. Table I shows the comparison of these values with Pauling's and with the experimental results.

TABLE I.

	E	D_e(e.v.)	$r_e(A)$	Z	Z'
This paper	−4.930	2.22	1.097	1.734	2.029
Pauling	−4.865	2.47	1.085	1.833	1.833
Experimental[2]	−5.00	2.5	1.090		

The writer wishes to thank Professor Pauling for valuable advice and Mr. Harker for checking some of the integrals.

[2] W. Weizel, *Bandenspektren* (Akad. Verlagsges. m.b.Z., Leipzig, 1931), pp. 255, 270.

Appendix

Most of the integrals occurring in this work can be calculated without much trouble. I_{14} required a somewhat laborious calculation by Sugiura's[3] method and I_{13} had to be expressed as a series which, however, converges very rapidly.

The functions H and S by means of which integrals I_6 and I_{13} are expressed have been discussed by several authors.[4, 5]

The integrals bearing the subscript ϵ are obtained from the integrals without this subscript by substituting $\epsilon\rho$ instead of ρ wherever ρ occurs.

$$s=\int\psi_1\varphi_1 d\tau_1=e^{-\rho}(1+\rho+\tfrac{1}{3}\rho^2),$$

$$t_0=\int\psi_1\xi_1 d\tau_1=\frac{8\epsilon^{3/2}}{(1+\epsilon)^3},$$

$$t=\int\psi_1\eta_1 d\tau_1=\frac{8\epsilon^{3/2}}{(1-\epsilon^2)^2}\left[\epsilon e^{-\rho}\left(1+\frac{4}{\rho(1-\epsilon^2)}\right)+e^{-\epsilon\rho}\left(1-\frac{4\epsilon}{\rho(1-\epsilon^2)}\right)\right],$$

$$F_1=\frac{1}{Z}\int\frac{\psi_1^2}{r_{B1}}d\tau=\frac{1}{\rho}-e^{-2\rho}\left(1+\frac{1}{\rho}\right),$$

$$F_2=\frac{1}{Z}\int\frac{\psi_1\varphi_1}{r_{A1}}d\tau=e^{-\rho}(1+\rho),$$

$$F_6=\frac{1}{Z}\int\frac{\psi_1\varphi_1\psi_2\varphi_2}{r_{12}}d\tau_1 d\tau_2=\frac{\rho^5}{15}[9H(2,2,\rho)-6H(2,0,\rho)+H(0,0,\rho)-3S(1,2,\rho)+S(1,0,\rho)],$$

$$F_7=\frac{1}{Z}\int\frac{\psi_1\xi_1}{r_{A1}}d\tau_1=\frac{4\epsilon^{3/2}}{(1+\epsilon)^2},$$

$$F_8=\frac{1}{Z}\int\frac{\psi_1\xi_1}{r_{B1}}d\tau_1=\frac{4\epsilon^{3/2}}{\rho(1+\epsilon)^3}\{2-e^{-(\epsilon+1)\rho}[(1+\epsilon)\rho+2]\},$$

$$F_9=\frac{1}{Z}\int\frac{\psi_1\eta_1}{r_{B1}}d\tau_1=\frac{4\epsilon^{3/2}}{\rho(1-\epsilon^2)^2}\{2e^{-\epsilon\rho}-e^{-\rho}[(1-\epsilon^2)\rho+2]\},$$

$$F_{10}=\frac{1}{Z}\int\frac{\psi_1\eta_1}{r_{A1}}d\tau_1=\frac{4\epsilon^{3/2}}{\rho(1-\epsilon^2)^2}\{2\epsilon e^{-\rho}+e^{-\epsilon\rho}[(1-\epsilon^2)\rho-2\epsilon]\},$$

$$F_{11}=\frac{1}{Z}\int\frac{\psi_1^2\eta_2^2}{r_{12}}d\tau_1 d\tau_2=\frac{1}{\rho}+\epsilon^3\left\{\frac{\epsilon e^{-2\rho}}{(\epsilon^2-1)^2}\left[-1-\frac{\epsilon^2-3}{(\epsilon^2-1)\rho}\right]\right.$$
$$\left.+e^{-2\epsilon\rho}\left[-\frac{1}{\epsilon^2}\left(1+\frac{1}{\epsilon\rho}\right)+\frac{1}{(\epsilon^2-1)^2}\left(\epsilon^2-2+\frac{\epsilon(\epsilon^2-3)}{(\epsilon^2-1)\rho}\right)\right]\right\},$$

$$F_{12}=\frac{1}{Z}\int\frac{\psi_1^2\psi_2\eta_2}{r_{12}}d\tau_1 d\tau_2=\frac{8\epsilon^{5/2}e^{-\rho}}{\rho(1-\epsilon^2)^2}+4\epsilon^{3/2}e^{-\epsilon\rho}\left[\frac{1}{1-\epsilon^2}-\frac{15-\epsilon^2}{(9-\epsilon^2)^2}-\frac{2\epsilon}{\rho}\left(\frac{1}{(1-\epsilon^2)^2}+\frac{\epsilon^2-21}{(9-\epsilon^2)^3}\right)\right]$$
$$+\frac{8\epsilon^{5/2}e^{-3\rho}}{(9-\epsilon^2)^2}\left(-1+\frac{\epsilon^2-21}{\rho}\right),$$

[3] Y. Sugiura, Zeits. f. Physik **45**, 484 (1927).
[4] N. Rosen, Phys. Rev. **38**, 2099 (1931).
[5] C. Zener and V. Guillemin, Phys. Rev. **34**, 999 (1929), etc.

$$F_{13}=\frac{1}{Z}\int\frac{\psi_1\eta_1\psi_2\eta_2}{r_{12}}d\tau_1 d\tau_2=\epsilon^3\rho^5\Big\{\frac{1}{15}[9H(2,2,\alpha\rho)-6H(2,0,\alpha\rho)+H(0,0,\alpha\rho)-3S(1,2,\alpha\rho)$$
$$+S(1,0,\alpha\rho)]+\frac{(\epsilon-1)^2\rho^2}{840}[7H(4,0,\alpha\rho)-47H(2,0,\alpha\rho)+9H(0,0,\alpha\rho)-21H(4,2,\alpha\rho)$$
$$+60H(2,2,\alpha\rho)+21S(1,4,\alpha\rho)+21S(3,2,\alpha\rho)-43S(1,2,\alpha\rho)-7S(3,0,\alpha\rho)+12S(1,0,\alpha\rho)$$
$$+50H(3,3,\alpha\rho)-60H(3,1,\alpha\rho)+18H(1,1,\alpha\rho)-100S(2,3,\alpha\rho)+50S(0,3,\alpha\rho)+60S(2,1,\alpha\rho)$$
$$-30S(0,1,\alpha\rho)]+\frac{(\epsilon-1)^4\rho^4}{192}\Big[\frac{1}{315}[-27H(4,2,\alpha\rho)+9H(4,0,\alpha\rho)+63H(2,2,\alpha\rho)-51H(2,0,\alpha\rho)$$
$$+10H(0,0,\alpha\rho)+27S(1,4,\alpha\rho)-54S(1,2,\alpha\rho)+15S(1,0,\alpha\rho)+27S(3,2,\alpha\rho)-9S(3,0,\alpha\rho)]$$
$$+\frac{2}{4725}[-675H(5,3,\alpha\rho)+2100H(3,3,\alpha\rho)+405H(5,1,\alpha\rho)-2385H(3,1,\alpha\rho)+675H(1,1,\alpha\rho)$$
$$-180S(0,5,\alpha\rho)+675S(2,5,\alpha\rho)+1642S(0,3,\alpha\rho)-3975S(2,3,\alpha\rho)+675S(4,3,\alpha\rho)$$
$$-1050S(0,1,\alpha\rho)+2358S(2,1,\alpha\rho)-405S(4,1,\alpha\rho)]+\frac{1}{2205}[6321H(4,4,\alpha\rho)$$
$$-14805H(4,2,\alpha\rho)+3465H(4,0,\alpha\rho)+9075H(2,2,\alpha\rho)-4545H(2,0,\alpha\rho)-621H(0,0,\alpha\rho)$$
$$+10591S(1,4,\alpha\rho)-12642S(3,4,\alpha\rho)-12810S(1,2,\alpha\rho)+14535S(3,2,\alpha\rho)+2949S(1,0,\alpha\rho)$$
$$-3465S(3,0,\alpha\rho)]\Big]+\cdots\Big\}\quad\text{where}\quad\alpha=\frac{1+\epsilon}{2},$$

$$F_{14}=\frac{1}{Z}\int\frac{\psi_1\varphi_1\xi_2\eta_2}{r_{12}}d\tau_1 d\tau_2=\frac{1}{5}\Big\{\epsilon e^{-(\epsilon+1)\rho}\Big(-\frac{\rho^3}{3}-\frac{6\epsilon^3+8\epsilon+4}{3\epsilon(\epsilon+1)}\rho^2-\frac{6\epsilon^2(\epsilon^2+\epsilon+1)+3\epsilon+2}{\epsilon^2(\epsilon+1)^2}\rho$$
$$+\frac{6\epsilon^5+6\epsilon^4-11\epsilon^3+10\epsilon^2+15\epsilon-1}{\epsilon^3(\epsilon+1)^3}\Big)+\frac{6}{\rho}\Big[ss_\epsilon\Big(C+\log(2\rho)-\log\frac{\epsilon+1}{\epsilon}\Big)$$
$$-[s_\epsilon s'Ei(-2\rho)+ss_\epsilon'Ei(-2\epsilon\rho)]+s's_\epsilon'Ei[-2(\epsilon+1)\rho]\Big]\Big\},$$

$$F_{15}=\frac{1}{Z}\int\frac{\psi_1\xi_1\psi_2\varphi_2}{r_{12}}d\tau_1 d\tau_2=\frac{8\epsilon^{3/2}e^{-\rho}}{(1+\epsilon)^3}(\rho+1)$$
$$+\frac{32\epsilon^{3/2}}{(1+\epsilon)^4(3+\epsilon)^2}\Big[e^{-\rho}\Big(-2\epsilon-5+\frac{6\epsilon+14}{(\epsilon+1)(\epsilon+3)\rho}\Big)-e^{-(2+\epsilon)\rho}\Big(1+\frac{6\epsilon+14}{(\epsilon+1)(\epsilon+3)\rho}\Big)\Big],$$

$$F_{16}=\frac{1}{Z}\int\frac{\psi_1\xi_1\varphi_2\eta_2}{r_{12}}d\tau_1 d\tau_2=\frac{64\epsilon^3}{(1+\epsilon^6)\rho}-\epsilon^3e^{-(\epsilon+1)\rho}\Big[\frac{64}{(1+\epsilon)^6\rho}+\frac{44}{(1+5)^5}+\frac{12\rho}{(1+\epsilon)^4}+\frac{4\rho^2}{3(1+\epsilon)^3}\Big].$$

The Kinetics of the Oxidation of Gaseous Glyoxal

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(Received June 25, 1935)

The kinetics of the oxidation of gaseous glyoxal have been investigated at 220°C. The reaction occurs by a chain mechanism, the rate being dependent upon roughly the second power of the aldehyde concentration, and independent of oxygen provided the oxygen concentration is not too low. The wall factor in the breaking of chains is not very pronounced, but the condition of the surface is of importance in the initiation of the chains. The main products of the reaction are CO, CO_2, H_2O and glyoxylic acid. The results are satisfactorily expressed by the mechanism of aldehyde oxidation previously proposed by Steacie, Hatcher and Rosenberg.

INTRODUCTION

THE oxidation of acetylene has been the subject of a considerable number of investigations, but the interpretation of the results obtained is still a matter of doubt. In the mechanisms which have been proposed glyoxal has been given a prominent place, since it has been frequently shown to be produced in considerable quantities.[1] For this reason it seemed to be advisable to investigate the decomposition and oxidation of glyoxal, since no data were available on its behavior. The results of the investigation of the decomposition have already been reported,[2] and the present paper deals with the kinetics of the oxidation.

The oxidation of glyoxal is also of interest by comparison with the behavior of acetaldehyde,[3] and of propionaldehyde.[4]

EXPERIMENTAL

The experimental method was identical with that of the previous investigation, except that since lower temperatures were required an oil bath was substituted for the electric furnace. The aldehyde and oxygen were mixed within the reaction vessel rather than outside it, since it had been found in the case of other aldehydes that incipient oxidation occurs even at room temperature.

[1] Kistiakowsky and Lenher, J. Am. Chem. Soc. **52**, 3785 (1930); Spence and Kistiakowsky, ibid. **52**, 4837 (1930); Lenher, ibid. **53**, 2962 (1931).

[2] Hatcher, Horwood and Steacie, J. Chem. Phys. **3**, 291 (1935).

[3] Bodenstein, Zeits. f. physik. Chemie **B12**, 141 (1931); Hatcher, Steacie and Howland, Can. J. Research **5**, 648 (1931); **7**, 149 (1932); Pease, J. Am. Chem. Soc. **55**, 2753 (1933).

[4] Steacie, Hatcher and Rosenberg, J. Phys. Chem. **38**, 1189 (1934).

THE PRESSURE CHANGE ACCOMPANYING THE REACTION

The reaction differed from the acetaldehyde and propionaldehyde oxidations in that instead of a decrease in pressure corresponding to the formation of a stable peracid, followed by a gradual increase in pressure at the end of the reaction, there was an increase throughout until a constant value was reached. The maximum pressure increases for typical experiments are shown in Table I. In most cases they represent the final pressure, which remained constant for from 1 to 15 hours. For the lower temperatures these values remain constant with varying oxygen/aldehyde ratio, but at 220°C there is a tendency to drift, which has very little apparent connection with the composition of the mixture, though when the oxygen/aldehyde ratio is lower than about 2 the pressure increases have a somewhat lower mean value. The significance of the pressure increase will be discussed later in connection with the mechanism of the reaction.

TABLE I. *Pressure increase at completion.*

T°C	$\frac{O_2}{CHO.CHO}$	INITIAL GLYOXAL PRESSURE (cm)	ΔP EXPRESSED AS % OF INITIAL GLYOXAL
150	2.13	11.50	28.3
150	1.68	11.90	29.8
200	2.74	14.45	43.9
200	1.05	14.25	42.8
220	3.82	12.00	91.2
220	3.78	9.00	78.9
220	3.22	15.00	83.7
220	2.95	11.95	85.3
220	2.94	8.95	81.5
220	2.74	12.10	90.0
220	2.26	15.10	86.7
220	1.83	12.10	81.5
220	1.75	12.00	67.9
220	1.65	12.10	72.7
220	1.54	12.10	71.5
220	1.29	12.00	75.8

The Products of the Reaction

The gaseous products of the reaction were withdrawn and analyzed as described in the previous paper. The first few analyses showed no hydrogen, and no combustions were done thereafter. The data for the actual analyses are given in Table II, and are recalculated in terms of the initial glyoxal in Table III. The method of determining the condensable matter was, as before, that of adding nitrogen. It will be seen that there is good agreement among the analyses in view of the smallness of the samples available.

Table II. *Gas analyses.* Temperature 220°C.

Expt. No.	Initial mixture (cm) CHO.CHO	O_2	N_2	Gaseous products (%) O_2	N_2	CO	CO_2
1	12.10	18.55	17.30	25.2	38.2	28.4	8.2
2	12.10	22.20	11.80	28.6	27.2	29.9	14.3
3	12.00	25.48	6.57	43.8	16.3	31.2	8.7
4	12.00	20.99	10.96	32.3	28.3	30.8	8.6
5	12.00	24.19	5.06	37.9	12.6	37.2	12.3
6	12.00	45.87	5.38	57.5	8.6	25.1	8.8
7	11.95	35.30	14.35	44.6	24.4	23.5	7.5
8	12.10	19.95	27.35	23.2	47.6	22.0	7.2

Table III. *The products of the reaction.*

Expt. No.	O_2 CHO.CHO	% ΔP at completion	Moles per 100 moles initial glyoxal O_2 used	CO	CO_2	Condensable	CO/CO_2
1	1.54	71.5	58.9	106.2	30.8	93.2	3.45
2	1.83	81.5	80.9	107.0	51.2	103.9	2.09
3	2.12	67.1	65.0	105.0	29.0	98.0	3.62
4	1.75	67.9	70.7	99.3	27.7	111.6	3.58
5	2.02	88.3	75.0	124.0	41.0	97.7	3.02
6	3.82	91.2	82.0	131.0	46.0	96.7	2.85
7	2.95	85.3	76.0	115.6	36.9	109.1	3.22
8	1.65	72.7	70.0	89.8	29.3	123.8	3.06

The average values for the eight analyses give the following overall equation for the reaction:

$$C_2H_2O_2+0.72O_2 = 0.37CO_2+1.10CO+1.04 \text{ Condensable.}$$

The average CO/CO_2 ratio is 2.98, and the average pressure increase 78 percent. From a material balance of this equation the empirical formula of the condensable material is found to be $C_{0.53}H_2O_{1.60}$.

To reconcile the possible products of the reaction with this formula it is necessary to assume that the carbon oxides are the result of complete combustion, so that the amount of water in the condensable material is half their sum. This leaves a residue of $C_{0.53}H_{0.53}O_{0.86}$. An obvious possibility on chemical grounds is glyoxylic acid, which has the formula, on the basis of the carbon above, $C_{0.53}H_{0.53}O_{0.80}$, and thereby satisfies the analyses almost perfectly.

The material balance offers little or no indication of a peroxidized end product, or of substances containing a higher proportion of oxygen than glyoxylic acid. The reaction bulb was cut down at the end of a run and an aqueous solution of the condensable products subjected to qualitative tests. It was strongly acid, gave a negative test for peracids with potassium iodide, and a negative reaction with Fehling's solution. The mercuric oxide test for formic acid gave a faint cloudiness hardly to be associated with metallic mercury, and was therefore considered to be negative. A decidedly positive test for glyoxylic acid was obtained by reversing the usual Hopkins-Cole test for tryptophane. It was found, however, that trimeric glyoxal reacts in the same way, and a trace of polymer might therefore be responsible for the positive result. However, since the test responded immediately, though it frequently took as long as 15 minutes with the reactants, and since the solution was strongly acid to litmus, it appears reasonable to accept the result of the test, at least as a partial verification of the inferences drawn from the material balance.

A blank run with glyoxal alone at the same temperature and for the average time to completion showed a pressure decrease due to polymerization of only three percent of the initial glyoxal. Under conditions of oxidation this would be considerably less, and may be quite safely ignored.

We can therefore account for the stable products empirically by assuming that glyoxal is oxidized directly or indirectly to glyoxylic acid, which is then largely oxidized completely to CO, CO_2 and water. The kinetic interpretation of the results will be discussed later.

The Rate of the Reaction

Complete data for some typical experiments are given in Table IV. The reaction shows a small induction period, as is usually the case in oxidation reactions.

TABLE IV. *Data for typical experiments.*

O_2/CHO.CHO	2.94		2.68		1.68	
$P_{CHO.CHO}$, cm	8.95		9.95		11.90	
TEMPERATURE	220°C		220°C		150°C	
REACTION VESSEL	Empty		Packed		Empty	
	TIME, (min.)	% ΔP	TIME, (min.)	% ΔP	TIME, (min.)	% ΔP
	0	0.0	0	0.0	0	0.0
	2	1.7	3	2.5	5	0.0
	4	4.5	6	3.5	10	0.4
	8	11.2	9	7.0	15	0.8
	10	15.6	16	12.6	20	1.3
	16	26.3	23	16.6	30	2.1
	34	49.8	38	22.1	40	3.8
	49	59.3	49	24.6	60	6.3
	79	69.4	90	30.2	80	10.5
	109	74.4	159	34.2	105	13.9
	192	80.5	214	34.7	151	18.1
	214	81.5	869	41.7		

TABLE V. *Reaction velocity data.* Temperature 220°C, unpacked reaction vessel.

GLYOXAL, (cm)	$\frac{O_2}{C_2H_2O_2}$	$T_{40}-T_{20}$, (min.)	GLYOXAL, (cm)	$\frac{O_2}{C_2H_2O_2}$	$T_{40}-T_{20}$, (min.)	
20	2.27	7.1	15	0.81	10.8	
20	1.87	7.3	10	3.44	10.2	
20	1.63	6.9	10	2.24	10.4	
20	1.59	6.7	10	1.67	9.9	
20	1.19	7.5	10	1.45	11.0	
20	0.93	7.5	10	1.26	11.5	
20	0.89	8.3	10	2.74	10.5	plus 20 cm N_2
20	0.78	8.8	10	2.39	10.9	plus 20 cm N_2
20	0.61	11.8	5	4.00	15.5	
20	0.53	11.3	5	3.22	15.5	
15	2.77	8.3	5	2.89	15.6	
15	2.36	8.1	5	2.41	17.2	
15	1.92	8.2	5	2.11	18.4	
15	1.33	8.4	5	2.09	18.5	
15	1.07	8.0	5	1.94	21.5	
15	0.96	9.4				

The rate of the reaction has been inferred from the rate of change of pressure. It is therefore necessary to show that under varying conditions a given pressure increase corresponds to the same amount of reaction. There are several indications that this is the case. In the first place, although the final pressure increases are rather erratic, there is no systematic variation with changing oxygen/glyoxal ratio. Secondly, the analyses at completion are in satisfactory agreement, and it therefore appears that the *final* result is the same no matter what relative concentrations of oxygen and glyoxal are used. That the course of the reaction is also the same is indicated by the fact that the form of the pressure-time curves does not change with changing oxygen/glyoxal ratio. Further confirmation is furnished by some analyses which were made when the pressure increase was 50 percent relative to the initial glyoxal. With oxygen/glyoxal ratios of 2.52, 2.18, 1.31 and 0.70 the CO/CO_2 ratios were sensibly constant, *viz.* 4.8, 4.6, 4.7 and 4.3. Thus it appears that at least the relative amounts of CO and CO_2 formed at any stage of the reaction are not appreciably dependent on the oxygen/glyoxal ratio. It therefore seems justifiable to use the time for the pressure to change from a 20 percent to a 40 percent increase as a measure of the rate of the reaction, and the data in Table V are reported in this manner.

At the beginning of a series of experiments with a new reaction vessel there was a pronounced surface aging effect, the velocity of the reaction increasing from run to run. It was usually necessary to make about 30 runs before reproducible results could be obtained. The data in Table V were obtained after the reaction vessel had reached a steady condition.

The effect of pressure

It will be seen from the above table that with glyoxal pressures of 20, 15 and 10 cm the rate is independent of the oxygen concentration provided that the oxygen/glyoxal ratio is greater than 1. The falling off in rate when the ratio is too low is hardly a real effect, since there is no longer sufficient oxygen for complete reaction. At the lowest glyoxal pressure (5 cm), however, the rate becomes dependent on the oxygen concentration when the oxygen/glyoxal ratio falls below about 2.5. By plotting the logarithms of the glyoxal pressures against the logarithms of $T_{40}-T_{20}$ we obtain a value for the order of the reaction of 1.6. Hence, except when the oxygen concentration is too low, we can express the rate by

$$-(d/dt)(C_2H_2O_2)=K(C_2H_2O_2)^{1\cdot 6}.$$

The effect of temperature

It is evident from the pressure increases at completion listed in Table I that the course of the reaction changes greatly with changing temperature. Under the circumstances it is hardly worth while determining the temperature coefficient, and measurements have therefore been confined to 220°C.

The effect of surface and of foreign gases

A number of experiments were made with a reaction vessel packed with short lengths of 3/16-inch Pyrex tubing which had been subjected to the same process of cleaning as the empty bulb. The packed bulb had a surface-volume ratio 5 to 6 times greater than the empty bulb. The reaction was slowed down considerably (about 50 percent), and there was a profound change in its course, the pressure increase at completion amounting to only 30 to 40 percent, and the CO/CO_2 ratio of the gaseous products being reduced from 3.0 to 1.7. It is apparent that the later stages of the reaction must be considerably altered. The magnitude of the retarding effect is not great, however, compared with other oxidation reactions, and it appears that the wall is not the major factor in breaking the reaction chains. This conclusion is supported by the experiments made with added nitrogen (Table V). It will be seen that no appreciable acceleration of the reaction is produced by the foreign gas, although such an acceleration would be expected if the majority of the chains were broken at the wall.

Discussion

The kinetic characteristics of the oxidation of glyoxal are strikingly similar to those of acetaldehyde, of propionaldehyde, and of oxidation reactions in general. The induction period, the dependence of the rate upon the aldehyde concentration to about the second power and its independence of oxygen, as well as the pronounced influence of the condition of the surface show that it must unquestionably occur by a chain mechanism. With acetaldehyde and propionaldehyde the chain carrier is an activated peracid, which is moderately stable after deactivation and appears among the condensable products at the end of the reaction, its formation leading to a decrease in pressure. With glyoxal an analysis in the induction period showed that some 30 percent of the average total oxygen consumption had occurred after three minutes of reaction, and a very small quantity of carbon monoxide was formed. It appears therefore that the mechanism is very similar to that of the other aldehydes. Glyoxal, however, is a comparatively unstable aldehyde, and it is not surprising to find that the intermediate chain carriers do not appear in the end products to any great extent. The reaction is therefore characterized by an increase in pressure, which is greater the higher the temperature. Formaldehyde[5] behaves in the same way.

The glyoxylic acid formed in the reaction probably arises by

$$\begin{array}{l} \mathrm{COOOH} \\ | \\ \mathrm{CHO} \end{array} + \begin{array}{l} \mathrm{CHO} \\ | \\ \mathrm{CHO} \end{array} = 2\begin{array}{l} \mathrm{COOH} \\ | \\ \mathrm{CHO} \end{array},$$

since peracids do not normally decompose to give the corresponding acid. The oxides of carbon may be assumed to arise in the usual way by the subsequent oxidation and decomposition of the primary products. The fact that the CO/CO_2 ratio decreases as the reaction proceeds, and that more CO_2 is formed in a packed reaction vessel indicates that the secondary processes leading to the formation of the oxides of carbon are at least partially heterogeneous.

That both aldehyde groups are not oxidized to the carboxylic structure is in agreement with the results of Hatcher and Holden,[6] who found no trace of oxalic acid during the oxidation of glyoxylic acid by hydrogen peroxide in aqueous solution.

The kinetic results are in excellent agreement with the mechanism proposed by Steacie, Hatcher and Rosenberg for the oxidation of gaseous aldehydes. Thus we have

$$R\mathrm{CHO} + \mathrm{O_2} = R\mathrm{COOOH}^* \quad (1)$$

$$R\mathrm{COOOH}^* + R\mathrm{CHO} = R\mathrm{COOOH} + R\mathrm{CHO}^* \quad (2)$$

$$R\mathrm{CHO}^* + \mathrm{O_2} = R\mathrm{COOOH}^* \quad (3)$$

$$R\mathrm{COOOH}^* + \mathrm{O_2} = R\mathrm{COOOH} + \mathrm{O_2} \quad (4)$$

$$R\mathrm{COOOH}^* = R\mathrm{COOOH}\ (\text{wall reaction}), \quad (5)$$

whence we obtain

$$-(d/dt)(R\mathrm{CHO}) = K_1K_2(R\mathrm{CHO})^2(\mathrm{O_2})/(K_4(\mathrm{O_2}) + K_5).$$

As we have seen, the wall effect is not large, but is nevertheless appreciable. Hence when the

[5] Fort and Hinshelwood, Proc. Roy. Soc. **A129**, 284 (1930); Askey, J. Am. Chem. Soc. **52**, 974 (1930).

[6] Hatcher and Holden, Trans. Roy. Soc. Can. (3) **19**, 11 (1925).

oxygen concentration is large K_w is negligible compared to $K_1(O_2)$, and the above expression reduces to

$$-(d/dt)(RCHO)=K_1K_2(RCHO)^2,$$

in agreement with experiment. On the other hand, we would expect that at low oxygen concentrations K_w would no longer be negligible, and that the rate would become dependent upon a power of the oxygen concentration lower than the first. Actually the data of Table V show that when the partial pressure of oxygen falls below about 10 cm the rate begins to fall off in the manner indicated above.

The bearing of these results upon the oxidation of acetylene will be discussed in a forthcoming publication.

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The Polarizability and Related Properties of Molecular Hydrogen and the Diatomic Hydrogen Ion

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The polarizability of molecular hydrogen is calculated from both the Rosen and the Wang eigenfunctions by the variational method. The eigenfunctions of the perturbed molecule contain two parameters which are adjusted to give the molecule a minimum energy. The Rosen eigenfunction leads to a parallel polarizability 7.5×10^{-25} cm^3 and a perpendicular polarizability 7.4×10^{-25} cm^3. The Wang eigenfunction gives similar results. When only one adjustable parameter is used in the variational method, the formula for the polarizability is $\alpha=8(\overline{q_1^2}+\overline{q_1q_2})^2a_0^3$ where q_1 and q_2 are the coordinates of electrons 1 and 2 in the direction of the applied electric field and a_0 is the radius of the first Bohr orbit of atomic hydrogen. The magnetic susceptibility and the mean square dimensions of the hydrogen molecule are computed. It is found that the Kirkwood formula is applicable to the diatomic hydrogen ion and polarizabilities are obtained for many internuclear separations using the Guillemin and Zener eigenfunction.

THE recent papers of Steensholt[1] have renewed interest in the problem of calculating the polarizability of molecular hydrogen. In 1932, we computed the polarizabilities by applying the variational method of Hylleraas[2] and Hassé[3] upon the Rosen[4] and Wang[5] eigenfunctions. The eigenfunctions for the perturbed molecule were considered in both the one parameter form: $\psi_0[1+A(q_1+q_2)]$ and the two parameter form: $\psi_0[1+A(q_1+q_2)+B(r_1q_1+r_2q_2)]$. Where ψ_0 is the eigenfunction of the unperturbed molecule. A and B are parameters to be varied so as to give the system a minimum energy; q_1 and q_2 are the coordinates of electrons one and two in the direction of the applied electric field as measured from the center of the molecule; r_1 and r_2 are their distances from the center of the molecule. The numerical results are presented in Table I and compared with the values obtained by Mrowka[6] and by Steensholt.[1] Mrowka formed approximate eigenfunctions for the excited states of the hydrogen molecule and applied the usual second-order perturbation method. Steensholt used the variational method with the Wang eigenfunction in the one-parameter form as given above. However, he took Wang's effective nuclear charge $Z_{\text{eff}}=1.166$, while we considered

TABLE I. *Polarizabilities in 10^{-25} cm^3.*

	$\alpha_\perp$	$\alpha_{\|\|}$	$\bar{\alpha}$	$\lvert\alpha_{\|\|}-\alpha_\perp\rvert$	$\partial\alpha_\perp/\partial R$	$\partial\alpha_{\|\|}/\partial R$
Rosen eigenfunc. 2 parameters	7.4	7.5	7.4	0.1	9.5×10^{-17} cm^2	11.0×10^{-17} cm^2
Rosen eigenfunc. 1 parameter	6.7	7.1	6.9	.4	8.0	10.8
Wang eigenfunc. 2 parameters	7.3	7.5	7.3	.2	9.8	10.2
Wang eigenfunc. 1 parameter	6.6	7.1	6.8	.5	8.9	10.2
Steensholt using Wang eigenfunc. and 1 parameter	5.2	7.7	6.0	2.5		
Mrowka	8.5	6.1	7.7	2.4		
Experimental			8.0	3.6		

[1] G. Steensholt, Zeits. f. Physik **93**, 620 (1935); **94**, 770 (1935).
[2] E. Hylleraas, Zeits. f. Physik **65**, 209 (1930).
[3] Hassé, Proc. Camb. Phil. Soc. **26**, 542 (1930); **27**, 66 (1931).
[4] N. Rosen, Phys. Rev. **38**, 2099 (1931).
[5] S. Wang, Phys. Rev. **31**, 579 (1928).
[6] B. Mrowka, Zeits. f. Physik **76**, 300 (1932).

$Z_{\text{eff}}=1.18$ which is more suited to the Rosen eigenfunction. This accounts for part of the discrepancy between our values. Mrowka found, in direct contradiction to the classical theory of Silberstein,[7] that the parallel polarizability of H_2 was smaller than the perpendicular. However, both Steensholt and this work find the parallel polarizability to be the larger. Van Vleck[8] has pointed out that the Hylleraas method is not strictly applicable to approximate eigenfunctions and may give results either too small or too large. The values for the polarizability therefore provide a very sensitive test of the eigenfunctions.

The polarizability using one parameter reduces to the simple form:

$$\alpha=8(\overline{q_1^2}+\overline{q_1q_2})^2a_0^3, \tag{1}$$

where the bars indicate the mean value. Since the electrons repel each other, $\overline{q_1q_2}$ should be negative. Actually, the Rosen and Wang eigenfunctions make this quantity zero for directions perpendicular to the line of nuclei and appreciable for the parallel direction. The dimensions of the hydrogen molecule may be calculated readily from the eigenfunctions. (z=direction parallel to line of nuclei, x and y are perpendicular.)

Eigenfunction	$\overline{z_1^2}$	$\overline{y_1^2}=\overline{x_1^2}$	$\overline{z_1z_2}$	$\overline{r_1^2}$
Rosen	$0.95a_0^2$	$0.76a_0^2$	$-0.17a_0^2$	$2.47a_0^2$
Wang	1.11	0.75	−0.33	2.61

Wang[9] made a direct calculation of $\overline{r_1^2}$ using his eigenfunction with the effective nuclear charge as discussed in the previous paragraph. He obtained: $\overline{r_1^2}=2.95a_0^2$ where a_0 is the "radius of the first Bohr orbit." The mean square values for the electronic radius may be used to calculate the diamagnetic susceptibility: $-Le^2\overline{r_1^2}/3mc^2$. Including the paramagnetic term as calculated by Van Vleck and Frank,[10] the total magnetic susceptibility is:

Eigenfunction	*Magnetic Susceptibility*
Rosen	-3.4×10^{-6} per mole
Wang	−3.6
Wang (calculation by Wang)	−4.2
Experimental	−3.9 to −4.0.

[7] Silberstein, Phil. Mag. **33**, 92, 215, 521 (1917).
[8] J. H. Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford Press, 1932), p. 205; also footnote at end of paper by Atanasoff, Phys. Rev. **36**, 1242 (1930).
[9] S. Wang, Proc. Nat. Acad. Sci. **13**, 798 (1927).
[10] Van Vleck and Frank, Proc. Nat. Acad. Sci. **15**, 579 (1929).

Polarizability of the Diatomic Hydrogen Ion

We have also calculated the polarizability of the diatomic hydrogen ion for various internuclear distances, using the Guillemin and Zener eigenfunction.[11] Steensholt[1] has recently carried through the calculation for the equilibrium distance. The method of Hylleraas and Hassé with one parameter leads directly to the Kirkwood[12] formula:

$$\alpha=4(\overline{q^2})^2a_0^3. \tag{2}$$

The following are our results: (in 10^{-25} cm^3)

R/a_0	$\alpha_\perp$	$\alpha_{\|\|}$	$\bar{\alpha}$	R/a_0	$\alpha_\perp$	$\alpha_{\|\|}$	$\bar{\alpha}$
0.1	0.4	0.4	0.4	2.0	2.5	7.2	4.0
1.0	1.1	1.7	1.3	3.0	4.1	26.7	11.6
				4.0	5.4	79.5	30

Steensholt obtained for $R=2.0$, the equilibrium distance:

$$\alpha_{\|\|}=7.7\times10^{-25}\text{ cm}^3,\qquad \alpha_\perp=2.4\times10^{-25}\text{ cm}^3,$$
$$\bar{\alpha}=4.2\times10^{-25}\text{ cm}^3.$$

When the nuclei become close, the polarizability approaches that of the helium ion. At large internuclear separations, the polarizability should become that of the hydrogen atom. However, the Guillemin and Zener eigenfunction does not approach the atomic eigenfunction and the parallel polarizability, as calculated from it, increases indefinitely as the nuclear separation increases. This is a striking example of the inadequacy of molecular orbital eigenfunctions at large internuclear distances. The dimensions of the diatomic hydrogen ion may be readily calculated:

R	$\overline{z^2}$	$\overline{x^2}=\overline{y^2}$	$\overline{r^2}$
$0.1a_0$	$0.26a_0^2$	$0.26a_0^2$	$0.78a_0^2$
1.0	.53	.43	1.40
2.0	1.11	.65	2.41
3.0	2.13	.83	3.80
4.0	3.68	.96	5.60

The writer wishes to express his gratitude to Professor E. U. Condon for suggesting this problem and directing the work.

[11] V. Guillemin and C. Zener, Proc. Nat. Acad. Sci. **15**, 4, 314 (1929).
[12] J. Kirkwood, Physik. Zeits. **33**, 2, 57 (1932).

Dielectric Investigations on Nitromethane and Chloropicrin

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The dielectric constants and densities of dilute solutions of nitromethane in heptane and of chloropicrin in heptane and in benzene have been measured and used to calculate the dipole moments of the solute molecules. The values thus calculated are considerably lower than those previously obtained in the gaseous state and are not well represented by the empirical equation of Müller. Measurement of the dielectric constant of pure liquid and solid nitromethane fails to show the existence of molecular rotation in the solid state. It is concluded, therefore, that the heavier molecule of chloropicrin does not rotate in the crystal.

AS IT seemed that dielectric constant measurements on nitromethane and chloropicrin in the solid, liquid and gaseous states would be of interest, the data contained in the present paper were obtained more than two years ago. The measurements on the gases have already been considered[1] in their bearing upon the problem of the structure of these and similar molecules. The measurements upon the liquid and solid states, which were made with newly purified materials, will be used to investigate the effect of solvent upon the apparent dipole moment and the possibility of dipole rotation in the crystal. Chloropicrin was not measured as a pure liquid or solid because the failure to find molecular rotation in solid nitromethane made it appear certain that the chloropicrin molecule with its much larger moment of inertia would not rotate in the crystal. The dielectric constants and densities were measured with apparatus previously described[2] as was the dielectric constant of pure nitromethane.[3] The refractive indices were measured with a Pulfrich refractometer.

Purification of Materials

Nitromethane

Material from the Eastman Kodak Company was distilled from phosphorus pentoxide and twice fractionally redistilled; m.p. −28.6°; b.p. 101.5° (762 mm); n_D^{25} 1.37970; d_4^{25} 1.1314.

Chloropicrin

Material from the Eastman Kodak Company was dried with calcium chloride and fractionally distilled, then redistilled under reduced pressure, the middle fraction being used; n_D^{25} 1.45956; d_4^{25} 1.6483.

Experimental Results

Dilute solutions of nitromethane in heptane and of chloropicrin in heptane and in benzene were measured. In Table I the first column gives the mole fraction c_2 of the polar substance in the solution and the succeeding columns give the values at 25° and 50° of the dielectric constants ϵ, the densities d of the solutions and the polariza-

TABLE I. *Dielectric constants, densities and polarizations.*

c_2	ϵ 25°	ϵ 50°	d 25°	d 50°	P_2 25°	P_2 50°
			Heptane-Nitromethane			
0.00000	1.920	1.884	0.6796	0.6579	(221.5	207.0 = P_∞)
.00633	1.965	1.924	.6804	.6587	216.3	203.6
.00857	1.980	1.938	.6807	.6590	212.0	201.5
.01005	1.990	1.947	.6809	.6592	210.7	199.8
.01095	1.996	1.953	.6810	.6593	209.0	200.8
.01795	2.043	1.997	.6820	.6602	203.4	197.8
.01934	2.053	2.006	.6821	.6603	203.7	197.5
.02037	2.060	2.012	.6822	.6604	203.5	196.6
.02808	2.112	2.060	.6834	.6615	198.8	193.1
.03936	2.188	2.132	.6848	.6628	193.6	189.8
			Heptane-Chloropicrin			
0.00000	1.920	1.884	0.6796	0.6579	(95.0	87.7 = P_∞)
.00835	1.941	1.902	.6850	.6633	95.7	87.3
.01752	1.964	1.922	.6911	.6692	94.5	87.7
.01852	1.966	1.924	.6917	.6698	94.0	87.6
.03866	2.017	1.968	.7050	.6827	93.3	87.2
.07103	2.103	2.042	.7268	.7038	93.0	87.3
.11071	2.213	2.141	.7542	.7305	92.0	87.4
			Benzene-Chloropicrin			
0.00000	2.274	2.224	0.8729	0.8460	(94.5	88.5 = P_∞)
.00560	2.298	2.245	.8775	.8505	94.5	89.2
.01304	2.331	2.273	.8841	.8568	93.4	88.1
.02646	2.389	2.323	.8956	.8680	92.4	86.8
.04604	2.475	2.398	.9125	.8844	91.4	86.5
.06068	2.538	2.453	.9248	.8965	90.4	85.7
.08188	2.628	2.534	.9429	.9141	88.9	85.0

[1] C. P. Smyth and K. B. McAlpine, J. Am. Chem. Soc. **56**, 1697 (1934).
[2] C. P. Smyth and W. S. Walls, J. Am. Chem. Soc. **53**, 527 (1931).
[3] C. P. Smyth and C. S. Hitchcock, J. Am. Chem. Soc. **54**, 4631 (1932).

TABLE II. *Refractions, orientation polarizations and dipole moments.*

Compound		CH_3NO_2	CCl_3NO_2	CCl_3NO_2
Solvent		C_7H_{16}	C_7H_{16}	C_6H_6
MR_D		12.49	27.29	27.29
$P_\infty - MR_D$	25°	209.0	67.7	67.2
	50°	194.5	60.4	61.2
$\mu_{sol.}(\times 10^{18})$obs.	25°	3.17	1.80	1.80
	50°	3.18	1.78	1.79
$\mu_{gas}(\times 10^{18})$calc.	25°	3.28	1.86	1.92
	50°	3.28	1.84	1.90
$\mu_{gas}(\times 10^{18})$obs.		3.42	1.88	1.88

tions P_2 of the polar substance. P_2 is obtained by use of the usual equations,

$$P_{12}=(\epsilon-1)(c_1M_1+c_2M_2)/(\epsilon+2)d$$

and

$$P_2=P_1+(P_{12}-P_1)/c_2,$$

in which P_{12} is the polarization of the mixture, and c_1 and c_2, M_1 and M_2 and P_1 and P_2 are, respectively, the mole fractions, molecular weights and polarizations of the individual components. These values of P_2 are extrapolated to infinite dilution to obtain P_∞, from which the dipole moment μ is obtained by means of the equation $\mu=0.0127\times10^{-18}\,[(P_\infty-MR_D)T]^{\frac{1}{2}}$, in which T is the absolute temperature and MR_D, the molar refraction, for the D sodium line, is calculated from the experimental values of n_D^{25} and d given under the "Purification of Materials." The values thus obtained are given in Table II together with moment values calculated from them for the gaseous state by an empirical equation and the previously observed values for the gaseous state. The dielectric constant values for solid and liquid nitromethane are shown in Table III, the frequency in kilocycles at which the measurement was made being given at the top of each column. Nearly half of the measurements are omitted for the sake of brevity. The conductance of the liquid was sufficient to cause some variation of the apparent dielectric constant with frequency, from which one would conclude that the values at 70 kc may be about 1 or 2 percent high, although they are considerably lower than those in *International Critical Tables*. The values for the solid are presumably low because of the presence of small cavities.

TABLE III. *Dielectric constant of pure nitromethane.*

Kc	70	30	12	7	3	1	0.7	0.4	0.3
t(°C)				SOLID (m.p. −28.6°)					
−90	3.39	3.39	3.39	3.39	3.39	3.39	3.39	3.39	3.39
−80	3.43	3.43	3.43	3.43	3.43	3.43	3.44	3.44	3.44
−70	3.48	3.48	3.47	3.48	3.47	3.48	3.49	3.49	3.49
−60	3.53	3.53	3.53	3.53	3.53	3.54	3.54	3.55	3.55
−50	3.59	3.59	3.59	3.59	3.59	3.60	3.61	3.63	3.63
−40	3.66	3.66	3.67	3.67	3.68	3.72	3.74	3.79	3.79
−35	3.72	3.72	3.73	3.74	3.75	3.82	3.85	3.90	3.91
−33	3.74	3.75	3.77	3.79	3.81	3.90	3.95	3.99	4.02
−31	3.78	3.80	3.83	3.86	3.94	4.05	4.13	4.22	4.28
−30	3.80	3.84	3.89	3.96	4.02	4.14	4.28	4.46	4.56
−29	3.93	3.93	3.99	4.05	4.15	4.36	4.56	4.87	5.02
		LIQUID							
−31.1	45.51	45.53	45.69						
−26.7	44.46	44.50	44.67						
−22.0	43.43	43.50	43.65						
−15.3	41.99	42.04	42.26						
−8.5	40.66	40.76	40.98						
2.9	38.57	38.68	38.97						
10.3	37.21	37.34	37.70						
19.0	35.79	35.95	36.35						
27.4	34.48	34.68	35.12						

DISCUSSION OF RESULTS

The differences between the dipole moment values in Table II at 25° and at 50° are no greater than the experimental errors. These apparent values of the moments are considerably lower than those found for the molecules in the gaseous state as commonly observed.[4] Various more or less empirical equations have been developed to represent the relation of the dielectric constant ϵ_1 of the solvent to the apparent polarization of the solute or the ratio of the moment $\mu_{sol.}$ found in solution to the moment μ_{gas} of the gas. The equation of Müller,[4] $\mu_{sol.}/\mu_{gas}=1-0.038\,(\epsilon_1-1)^2$, gives the calculated values in Table II. As the experimentally observed values of chloropicrin in the two solvents are indistinguishable, the equation gives a difference of 0.06 between the two values calculated for the gas, which is unsatisfactory. The mean of the gas values calculated from the two sets of solutions is identical with the value observed for the gas. The equation seems, therefore, to be a not bad approximation for chloropicrin. For nitromethane, the equation gives a calculated gas value less than half of the way up to the observed value for the gas and must, accordingly, be regarded as inadequate in this case. As a matter of fact, this is not at all surprising since its applicability has been known to be limited[5] and Müller and Mortier[6] in a recent paper show several different types of solvent effect upon polarization. The equation works admirably for nitrobenzene,[7] but the exceptionally

[4] See H. Müller, Physik. Zeits. **34**, 689 (1933) and others.
[5] Cf. C. P. Smyth and K. B. McAlpine, J. Chem. Phys. **3**, 347 (1935).
[6] Müller and Mortier, Physik. Zeits. **36**, 371 (1935).
[7] K. B. McAlpine and C. P. Smyth, J. Chem. Phys. 3, 55 (1935).

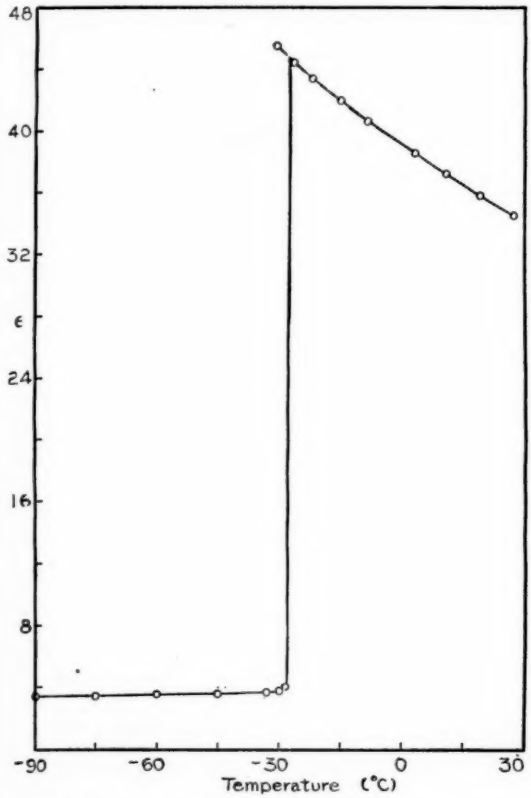

FIG. 1. Variation with temperature of the dielectric constant of nitromethane at 70 kc.

strong field of force which must exist around the small nitromethane molecule with its large dipole moment may well cause behavior different from that of a molecule larger in size or smaller in moment.

The variation with temperature of the dielectric constant of pure nitromethane shown in Table III and Fig. 1, which gives the values at a frequency of 70 kc, is very similar to that previously found for nitrobenzene and leads to similar conclusions. What looks, at first glance, like a slight anomalous dispersion in the values in Table III is presumably the effect of the presence of a small quantity of impurity, which causes traces of liquid to remain in the solid near the melting point. As in the case of nitrobenzene, there is no change in the course of the curve for the liquid in the neighborhood of the freezing point, even when supercooled as much as 2.5° below it, which indicates that there is no suddenly increased formation of molecular aggregates in this region, since such formation would almost certainly alter greatly the effect of the large dipoles in the molecules and so radically affect the curve. The tremendous drop in dielectric constant on solidification to a value normal for a solid in which there is no appreciable effect of dipoles or ionic charges indicates that there is little or no dipole rotation in the solid. This proves the absence in the crystal of rotation of the molecule about any axis perpendicular to the line passing through the carbon and nitrogen nuclei, in which the molecular dipole lies, but does not prove the absence of rotation around this line as axis, about which the molecule would have its smallest moment of inertia. The methyl alcohol molecule, which must have a much smaller moment of inertia around an axis close to the line through the carbon and oxygen nuclei, shows dipole rotation between $-114.0°$ and the melting point,[8] which further measurements indicate to be rotation of the entire molecule.[9] As the moment of inertia of the nitromethane molecule around an axis perpendicular to the carbon-nitrogen line is much larger than most, if not all, of the moments of inertia involved where the existence of molecular rotation has been clearly established and as the large dipole moment of the molecule should also tend to make the energy necessary for rotation around such an axis large, the failure to find rotation in this case is in conformity with our ideas of molecular rotation in solids. In other words, molecular rotation in a solid is very improbable unless the moment of inertia involved in the rotation is small and the internal field weak.

[8] C. P. Smyth and C. S. Hitchcock, J. Am. Chem. Soc. **56**, 1084 (1934).

[9] Paper by S. A. McNeight and C. P. Smyth presented to the Division of Physical and Inorganic Chemistry of the American Chemical Society, New York, April 26, 1935.

The Electronic Structure of Diamond

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The method of Wigner, Seitz and Slater has been applied to the determination of the electronic structure of diamond. It is found that the energy levels of the carbon atom are broadened into bands similar to the energy bands in metals. The $2s$ level of the atom splits into two bands, and the $2p$ level into six bands. The two $2s$ bands are completely filled by electrons and the two lowest of the $2p$ bands. The lowest unfilled band has a much higher energy than the highest filled band. The lack of electrical conductivity is explained and other properties of the diamond are discussed.

ALTHOUGH Hund[1] has given a very good qualitative discussion of the properties of crystals of all types in relation to their electronic structure, quantitative discussion of the electronic eigenfunctions in crystals has been confined to metals. Three methods have been devised to treat these problems. In the free electron model, it is assumed that to a first approximation the eigenfunctions are those of free electrons, and the potentials of the nuclei and other electrons are treated as a perturbation. In the method of Bloch, the electrons are assumed as a first approximation to be in states represented by linear combinations of atomic eigenfunctions. Finally, in the method of Wigner and Seitz, the crystal is divided into cells of approximately spherical shape. Eigenfunctions are then found which satisfy Schrödinger's equation within these cells and which are joined smoothly at the cell boundaries.[2]

In this paper the method of Wigner and Seitz, as extended by Slater, has been applied to diamond, chosen as the most typical nonmetallic crystal, with the object of explaining the characteristic differences between metals and nonmetals.

The crystal structure of diamond, as determined by W. H. and W. L. Bragg,[3] is face-centered cubic with two atoms in the unit cell. If we locate one atom at the origin of a Cartesian coordinate system, and the second atom of the cell at (a, a, a), the whole lattice may be generated by translating these atoms by vectors of the form $n_1\mathbf{v}_1+n_2\mathbf{v}_2+n_3\mathbf{v}_3$, where the components of $\mathbf{v}_1$ are $0, 2a, 2a$, those of $\mathbf{v}_2$ are $2a, 0, 2a$, and those of $\mathbf{v}_3$ are $2a, 2a, 0$, while n_1, n_2, and n_3 are arbitrary integers. Each atom of the lattice is surrounded by four nearest neighbors at a distance $2R=\sqrt{3}\ a$. It is found experimentally that $a=0.89\text{A}=1.69$ Bohr radii.

In order to apply the method of Wigner and Seitz it is necessary to surround each atom by a cell formed by planes bisecting the lines joining the atom to its neighbors. In the diamond structure the planes bisecting the lines joining any atom to its four nearest neighbors form a regular tetrahedron. The twelve planes bisecting the lines to the next nearest neighbors cut off the corners of this tetrahedron, leaving a 16-sided solid, illustrated in Fig. 1. The cells surrounding the two atoms of the unit cell of the crystal are identical, but are oppositely oriented.

To join the eigenfunctions at all 16 faces of these cells is so complicated that it is impracticable. It was therefore decided to fit the eigenfunctions so that the value and normal derivative would be continuous at the four points midway between the atom and its nearest neighbors, that is, at the centers of the hexagonal faces of the cell.

Since there are two atoms in the unit cells of the crystal this joining must be carried out for two Wigner-Seitz cells simultaneously. If we take as our two cells those surrounding the atoms at $(0, 0, 0)$ and (a, a, a) the joining points for the first cell are $P_1=(a/2, a/2, a/2)$, $P_2=(a/2, -a/2, -a/2)$, $P_3=(-a/2, a/2, -a/2)$, and $P_4=(-a/2, -a/2, a/2)$. For the second cell the joining points are $P_5=(a/2, a/2, a/2)$, $P_6=(a/2, 3a/2, 3a/2)$, $P_7=(3a/2, a/2, 3a/2)$, and $P_8=(3a/2, 3a/2, a/2)$. (P_1 and P_5 coincide of course, but it is convenient

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[1] Papers and Discussions of the Int. Conf. Phys., London, 1934. Vol. II, p. 36 (Published by the Physical Society, London).

[2] These methods are described in detail and with complete literature references in a review by J. C. Slater, Rev. Mod. Phys. **6**, 210 (1934).

[3] Bragg, Proc. Roy. Soc. **A89**, 277 (1913).

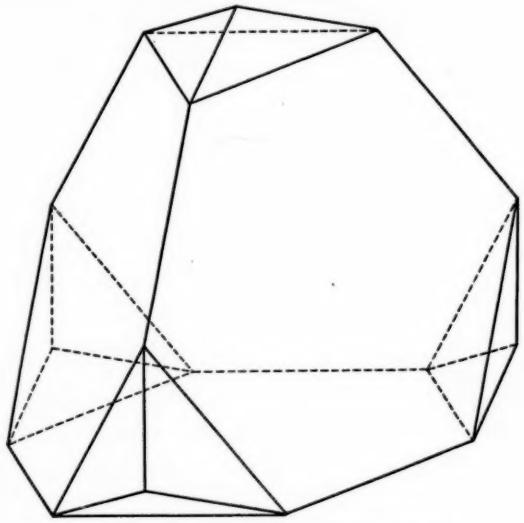

FIG. 1. The Wigner-Seitz cell for diamond.

to have different notations when regarding the point as in the first or second cell.)

The requirement that the eigenfunction have the same value at P_1 as at P_5 involves one condition on the eigenfunction. Since P_6 is translated from P_2 by the lattice vector $\mathbf{v}_1$, the usual Bloch condition requires that the value of the eigenfunction at P_6 be the value at P_2 multiplied by a factor $\exp i\mathbf{k}\cdot\mathbf{v}_1$, where $\mathbf{k}$ is an arbitrary vector determining the wavelength and direction of the electron wave through the crystal. Similarly the value of the eigenfunction at P_7 must be the value at P_3 multiplied by $\exp i\mathbf{k}\cdot\mathbf{v}_2$ and the value at P_8 must be the value at P_4 multiplied by $\exp i\mathbf{k}\cdot\mathbf{v}_3$. These four conditions, plus the four similar conditions on the derivative of the eigenfunction, make eight conditions in all which must be satisfied by the eigenfunctions in the two cells.

If we choose eight eigenfunctions $\psi_1, \psi_2, \cdots, \psi_8$, and assume that our final eigenfunction is a linear combination of the form

$$\begin{aligned}\Psi = {} & iA\psi_1 + iB\psi_2 + iC\psi_3 + iD\psi_4 \\ & + E\psi_5 + F\psi_6 + G\psi_7 + H\psi_8,\end{aligned}$$

where $A, B, \cdots, H$ are constants, then the eight conditions are just sufficient to determine the eight constants. (The factor i has been introduced for later convenience.) The eight eigenfunctions chosen were constructed from an s eigenfunction and three p eigenfunctions for each of the two atoms. The exact functions are shown in Table I. In this table $S(r)$ is the s eigenfunction and $P(r)$ the radial part of the p eigenfunction of an electron of energy E in the field of an ionized carbon atom. x, y, z are Cartesian coordinates with origin at (0, 0, 0) and r is the distance from (0, 0, 0). x', y', z' and r' have corresponding significance with respect to the point (a, a, a).

TABLE I.

EIGENFUNCTION	VALUE IN CELL ABOUT (0, 0, 0)	VALUE IN CELL ABOUT (a, a, a)
ψ_1	$S(r)$	$-S(r')$
ψ_2	$\sqrt{3}(x/r)P(r)$	$\sqrt{3}(x'/r')P(r')$
ψ_3	$\sqrt{3}(y/r)P(r)$	$\sqrt{3}(y'/r')P(r')$
ψ_4	$\sqrt{3}(z/r)P(r)$	$\sqrt{3}(z'/r')P(r')$
ψ_5	$S(r)$	$S(r')$
ψ_6	$\sqrt{3}(x/r)P(r)$	$-\sqrt{3}(x'/r')P(r')$
ψ_7	$\sqrt{3}(y/r)P(r)$	$-\sqrt{3}(y'/r')P(r')$
ψ_8	$\sqrt{3}(z/r)P(r)$	$-\sqrt{3}(z'/r')P(r')$

The eight equations of continuity of value and derivative may then be written in the form[4]

$$\begin{aligned}
sA + {} & p(B + C + D) = 0 && \text{(1a)}\\
sA + {} & p(B - C - D) + KsE + Kp(F - G - H) = 0 && \text{(1b)}\\
sA + {} & p(-B + C - D) + LsE + Lp(-F + G - H) = 0 && \text{(1c)}\\
sA + {} & p(-B - C + D) + MsE + Mp(-F - G + H) = 0 && \text{(1d)}\\
& s'E + p'(F + G + H) = 0 && \text{(1e)}\\
-Ks'A - Kp'(B - C - D) + {} & s'E + p'(F - G - H) = 0 && \text{(1f)}\\
-Ls'A - Lp'(-B + C - D) + {} & s'E + p'(-F + G - H) = 0 && \text{(1g)}\\
-Ms'A - Mp'(-B - C + D) + {} & s'E + p'(-F - G + H) = 0, && \text{(1h)}
\end{aligned}$$

where $s = S(R)$, $s' = (dS/dr)_{r=R}$, $p = P(R)$, $p' = (dP/dr)_{r=R}$. K, L and M are defined by $K = \tan(\mathbf{k}\cdot\mathbf{v}_1/2)$, $L = \tan(\mathbf{k}\cdot\mathbf{v}_2/2)$ and $M = \tan(\mathbf{k}\cdot\mathbf{v}_3/2)$.

In order that $A, B, \cdots, H$ shall not all vanish it is necessary that the determinant of the coefficients vanish. The vanishing of this determinant gives one relation between K, L, M and hence between the components of $\mathbf{k}$, since s, s', p and p' are fixed if E and a are fixed. Thus if the direction of $\mathbf{k}$ is chosen, its magnitude is determined.

[4] The derivation of these equations is exactly similar to the reduction used by Slater, Phys. Rev. **45**, 796 (1934).

Unfortunately it is not feasible to solve this determinantal equation in general.

If, however, the direction of **k** is chosen to lie in the plane $x=y$ it becomes possible to reduce Eqs. (1). If **k** lies in this plane, $K=L$. Placing $L=K$ in Eqs. (1), add and subtract Eqs. (1b) and (1c), and Eqs. (1f) and (1g). Letting $B+C=U$, $B-C=V$, $F+G=X$, and $F-G=Y$ Eqs. (1) become

$$
\begin{aligned}
&sA + pU + pD = 0 && (2a)\\
&sA - pD + Ks E - Kp H = 0 && (2b)\\
&sA - pU + pD + Ms E - Mp X + Mp H = 0 && (2c)\\
&-Ks'A + Ks'D + s'E - p'H = 0 && (2d)\\
&-Ms'A + Mp'U - MpD' + s'E - p'X + p'H = 0 && (2e)\\
&s'E + p'X + p'H = 0 && (2f)
\end{aligned}
$$

$$
\begin{aligned}
&pV + Kp Y = 0 && (3a)\\
&-Kp'V + p'Y = 0. && (3b)
\end{aligned}
$$

Unless p or $p'=0$ Eqs. (3) require $V=Y=0$ for all real K. In order that A, U, D, E, X and H do not all vanish we must have

$$
\begin{vmatrix}
s & p & p & 0 & 0 & 0\\
s & 0 & -p & Ks & 0 & -Kp\\
s & -p & p & Ms & -Mp & Mp\\
-Ks' & 0 & Kp' & s' & 0 & -p'\\
-Ms' & Mp' & -Mp' & s' & -p' & p'\\
0 & 0 & 0 & s' & p' & p'
\end{vmatrix} = 0. \quad (4)
$$

If we let $\mu=sp'/s'p$ this equation reduces to

$$
(\mu+3)(3\mu+1)K^2M^2+4(\mu+1)^2K^2-4(\mu-1)^2KM + (\mu+3)(3\mu+1)M^2+16\mu=0. \quad (5)
$$

Finally if we let $\omega=(\mu^2+1)/\mu$ we may put this equation into the form

$$
\omega=\frac{-(10K^2M^2+8K^2+8KM+10M^2+16)}{3K^2M^2+4K^2-4KM+3M^2}. \quad (6)
$$

Thus ω can be evaluated directly from **k**. By means of a plot of ω against the energy E, the value of E can therefore be found from **k**.

Construction of such a plot of ω against E involves the determination of s, s', p and p' for a number of values of E. These values were computed by numerical integration of the radial part of Schrödinger's equation. As a first approximation to the potential field inside the cell, the potential calculated from the eigenfunctions of the free carbon atom calculated by Torrance[5] was used. From the results of a series of numerical integrations s, s', p and p' were found as a function of E for a range of values of a. In Fig. 2 the results are shown in a plot of E against R. The equation of curve I is $s'=0$; curve II, $s/s'+p/p'=0$; curve III, $s=0$; curve IV, $p'=0$; curve V, $s/s'+p/p'=0$; and curve VI, $p=0$.

When E is found as a function of **k** using Eq. (6) it is found that to each value of **k** there correspond four values of E. One of these values lies in the diagonally shaded region bounded by curves I and II in Fig. 2; the second in the vertically shaded region bounded by curves II, III and IV; the third in the horizontally shaded region bounded by curves III, IV and V; and the fourth in the diagonally shaded region between curves V and VI. Besides these values of E it is found that Eqs. (2) are satisfied by any value of **k** if either $p=0$ or $p'=0$ and Eqs. (3) are also satisfied for any **k** if $p=0$ or $p'=0$.

Thus for any value of **k** there are eight possible eigenfunctions, two pairs being degenerate. Fig. 2 shows that as the internuclear distance is increased the two lowest bands of energy levels go over into the $2s$ level of the carbon atom, while the other six bands go over into the $2p$ level. Now at infinite separation the $2s$ level contains two electrons, so that it is reasonable to suppose that each band will be filled by one electron per atom. A calculation of the type given by Slater[6] confirms this argument. Since there are four electrons per atom in carbon (neglecting the $1s$ electrons) the normal state of the crystal will have the two $2s$ bands filled and the two lowest $2p$ bands, i.e., the two degenerate bands following curve IV in Fig. 2. The energies of all these bands are lowest in the neighborhood of the observed internuclear distance ($R=1.46$ Bohr radii).

While the calculations made with the atomic potential field are probably reasonably accurate

[5] Torrance, Phys. Rev. **46**, 388 (1934).

[6] Slater, Rev. Mod. Phys. **6**, 276 (1934).

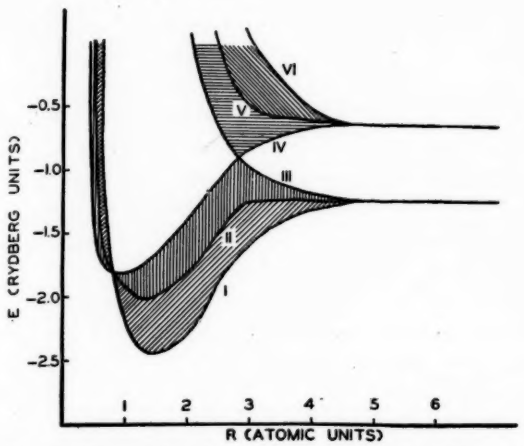

FIG. 2. Energy bands in diamond as a function of R (one-half the internuclear distance). Besides the four shaded bands, there are four bands of zero width, two following curve IV and two following curve VI.

for large internuclear distances, the crowding of electrons toward the nucleus when the interatomic distance is small undoubtedly produces serious changes in the potential field. For this reason a second approximation to the field was made for the particular distance $R=1.44$. In this calculation, however, a difficulty arises with the additive constant occurring in the potential. A number of choices are possible for this constant. The usual choice is to fix this constant in such a way that the energy levels of the inner shells of electrons are not changed. In this case, however, this procedure would lead to too low a value for the total energy, for there are four electrons being crowded into a nucleus whose charge is only six electronic units. A rough calculation shows that the effective nuclear charge may be changed by as much as two units, or 33 percent, hardly a negligible change.

A second way in which the constant might be fixed would be to assume that the field due to the crystal outside the cell in question is zero, so that the potential at the surface of the cell is e/R. The energy obtained by the first choice is too low, that from the second choice is too high. It seems impossible to determine a reasonable choice of this constant without a complete evaluation of the energy in the way outlined by Slater.[7]

The eigenfunctions calculated from the second approximation to the potential lead to the relation between E and $\mathbf{k}$ shown in Fig. 3 for values of $\mathbf{k}$ lying in the plane $x=y$. In this figure $k_x=k_y$ is plotted as abscissa and k_z as ordinate, while the values of E are shown by contours. The E values are those determined by the second choice of the additive constant in the potential. The first choice would lower all values by 2.3 Rydberg units. In the inner part of the figure are shown the E values of the lowest energy band. Because of the periodicity of E as a function of $\mathbf{k}$, this inner figure could be extended over the whole plane, but for convenience the adjacent portions are used to show the contours arising from the second band. It will be seen that for waves traveling in the z direction there is no discontinuity in energy in passing from the lowest to the second band, but that for any other direction in the plane there is a gap between bands. The degenerate bands following curve IV in Fig. 2 are indicated in the outermost portion of the diagram.

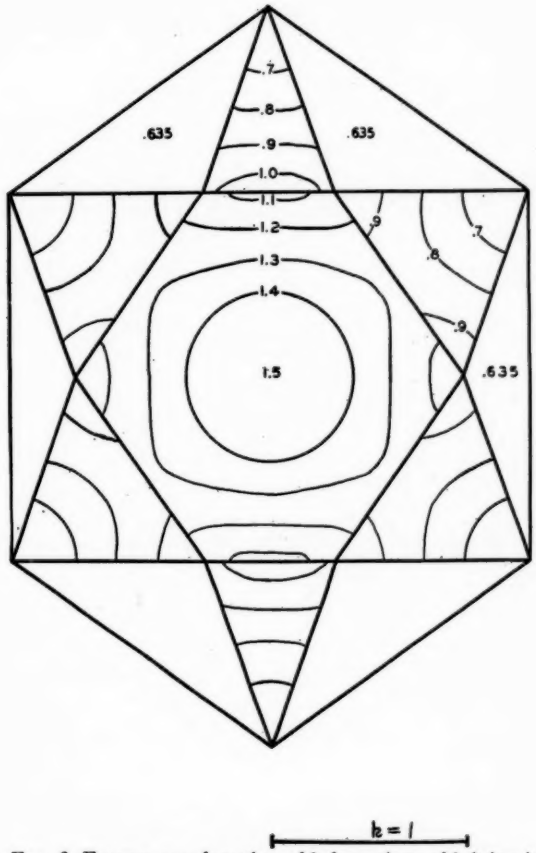

FIG. 3. Energy as a function of $\mathbf{k}$ for values of $\mathbf{k}$ lying in the plane $x=y$. The contours give $-E$ in Rydberg units.

[7] Slater, Rev. Mod. Phys. 6, 263 (1934).

For the eigenfunctions of these bands the energy has the same value for all values of **k**.

Although not very much of a quantitative nature can be concluded from these results, the essential differences between diamond and the metals are apparent. In a metal there is always an energy band which is not completely filled. As the various workers on metals have shown, the electrical conductivity is a direct consequence of this fact. In the diamond the low energy bands are all completely filled, and a large amount of energy would be necessary to promote an electron to an unfilled band. Now in each band, for every electron wave traveling in one direction there is a second wave of the same energy traveling in the opposite direction. The net result is that a filled band can produce no flow of charge. Hence it follows that the diamond is a nonconductor.

Some conclusions can be drawn with respect to the absorption spectrum. At the normal internuclear distance the curve III has risen to such a high energy that transitions of electrons from the filled bands to the band lying above it would take more energy than the ionization potential of the normal carbon atom. It is almost certain that some band arising from the $3d$ level of the carbon atom will have a lower energy. If ultraviolet light is absorbed by diamond it is most probable that the transition which actually takes place is one to such a level. Peter[8] has measured the absorption coefficient and refractive index of diamond down to 2260A. No absorption bands were found, but extrapolation of the dispersion curve indicates an absorption band in the neighborhood of 1750A, corresponding to an excitation energy of about 7 electron volts. This value seems too low for a transition to a $2p$ band, and therefore is almost certainly evidence of a low $3d$ band.

An interesting feature of the eigenfunctions of the diamond is the change in character of the eigenfunctions of the second lowest band as the internuclear distance is decreased. For large separations the eigenfunctions of this band are s-like in character, but after the point of intersection of curves III and IV (Fig. 2) has been passed the eigenfunctions have essentially the character of p functions. This change in character is essentially the promotion which Heitler and London have postulated to account for the quadrivalence of carbon. There is, however, no sign of the combination of s and p eigenfunctions into the "tetrahedral" eigenfunctions postulated by Slater and Pauling to account for the phenomena of directed valence observed in carbon.

The author wishes to express his deep appreciation to Professor J. C. Slater for his assistance and discussions of this problem.

[8] Peter, Zeits. f. Physik **15**, 358 (1923).

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Electronic Structures of Molecules
X. Aldehydes, Ketones and Related Molecules

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Electron configurations for the normal states of H_2CO, CH_3HCO, Cl_2CO are explicitly given, also for the low excited states of H_2CO. The structures, ionization potentials, and longest wavelength electronic band spectra of these and other related or analogous molecules (saturated aldehydes, ketones, thioaldehydes, thioketones, etc.) are interpreted in relation to these configurations. In particular is it shown that the minimum ionization potential of $\rangle C=O$ or $\rangle C=S$ corresponds to removal of a nonbonding $2p$ electron from the O atom or a nonbonding $3p$ from the S atom, unless the groups attached to the C contain other unusually easily ionized electrons. Similarly, the longest wavelength band system, commonly attributed to the C=O (or C=S) double bond, corresponds to excitation of the nonbonding $2p_O$ or $3p_S$ to an excited orbital which is largely but probably not quite wholly localized in the C=O or C=S bond, and which has C↔O or C↔S antibonding power, i.e., loosens the bond somewhat. This excitation process is responsible for color in the $\rangle C=S$ compounds. The C=O (or C=S) bond is a true double bond in the sense that the binding is effected essentially by two pairs of C−O (or C−S) bonding electrons. The C=O bond is essentially the same also in saturated monobasic acids RCOOH or at least in their esters.

1. Normal State and Ionization Potential of Formaldehyde

THE aldehydes RHC=O and the ketones R′RC=O can be considered as derivatives of formaldehyde H_2CO (R=alkyl radical, or derivative thereof). Various other molecules such as $Cl_2C=O$, $Cl_2C=S$, RHCS, R_2CS can also be considered as derivatives or analogs of H_2CO. Even organic acids R(OH)C=O and the derivatives can to a considerable extent be forced into this category.

Common to the absorption spectra of all the aldehydes and ketones is a band system near λ2900, often showing fine structure. This is generally agreed to be associated with the presence of the C=O bond. A second, much more intense, absorption system appears near λ1900 in all aldehydes and ketones, except formaldehyde where it is apparently displaced to about λ1600 or λ1700. This second system seems also to be definitely associated with the presence of the C=O bond, as was pointed out to the writer by Dr. C. P. Snow in correspondence.

Except possibly in respect to the anomaly in the second system, formaldehyde may reasonably be taken as prototype for the aldehydes and ketones. In seeking to predict its electronic structure, we may note that it is isoelectronic with, and in a sense is intermediate between, O=O and $H_2C=CH_2$, just as, e.g., CH_3I stands between I_2 and C_2H_6, or CH_3NH_2 between N_2H_4 and C_2H_6 (cf. earlier papers[1, 2]). As regards symmetry, $H_2C=O$ (symmetry C_{2v}) is closer to C_2H_4 (symmetry V_h) than to O_2 (symmetry $D_{\infty d}$), but inferior to both. Strong polarity is to be expected in the CO bond, and distinctly weaker polarities in the C−H bonds.

On due consideration, taking cognizance of what is known (see below) about the ultraviolet spectrum and I (the ionization potential), one arrives at the following electronic structure (1s electrons of C and O are omitted):

$$(2s)^2[sa_1]^2[x_O+x_C,\ b_1]^2[yb_2]^2[z_O+z_{CH_2},\ a_1]^2(2p_yb_2)^2,\ {}^1A_1.$$

approx. loc.	OH_2CO	O−C	CH_2	O−CH_2	O	(1)
vert. I	(32) (22)	(15.5)	(15.5)	(15?)	11	

The I values in parentheses are *estimated* values, the other is observed. Axes z, x, y, are, respectively, along the symmetry axis, perpendicular to the plane of the molecule, and in the latter perpendicular to the symmetry axis. The 2s and $2p_y$ orbitals are, probably to a good approximation, nonbonding O atom orbitals. All the other orbitals have either C−O or C−H bonding properties, or both.

Configuration (1) is similar to the normal state configuration[2] of C_2H_4, except that one CH_2 group with its intraradical[1] orbital $[yb_2]$ have been replaced by the O atom with its nonbonding orbital $2p_yb_2$. The orbital $[x_O+x_C]$ here corresponds to $[x+x]$ in C_2H_4, and is strictly confined to the C−O bond, just as $[x+x]$ is to the C−C bond. It differs from the latter in being strongly polar, i.e., $[x_O+x_C]$ really means, in LCAO approximation,[3]

$$a(2p_x)_O+b(2p_x)_C,$$

with $a>b$ rather strongly, since O is much more electronegative than $2p_C$.[4]

The orbitals (2s), $[s]$, and $[z_O+z_{CH_2}]$ here (all of type a_1) correspond to $[s+s,\ a_{1g}]$, $[s-s,\ b_{1u}]$, and $[\sigma+\sigma,\ a_{1g}]$ of C_2H_4 (z here means $2p_z$, as does σ for C_2H_4). There is, however, not a one to one correspondence. All that is definitely obvious about the forms of (2s), $[s]$ and $[z_O+z_{CH_2}]$ is that in LCAO approximation they represent three of the four solutions of a perturbation problem starting from $2s_O$, $[s]_{CH_2}$, $(2p_z)_O$ and $[z]_{CH_2}$. Roughly, since the effective term value[4] of unperturbed $2s_O$ is much larger than that of $[s]_{CH_2}$, etc., the lowest-energy solution is just $2s_O$, as is indicated in (1). The orbital of next lowest energy is probably one built primarily on $[s]_{CH_2}$ but with a considerable admixture of $(2p_z)_O$, together with more or less of $[z]_{CH_2}$ and $(2s)_O$; this mixture is designated simply $[s]$ in (1). Its bonding power should be more or less divided between C−H and C−O

[1] R. S. Mulliken, J. Chem. Phys. 3, 506 (1935): VII of this series.
[2] R. S. Mulliken, J. Chem. Phys. 3, 517 (1935): IX.
[3] R. S. Mulliken, J. Chem. Phys. 3, 375 (1935): VI.
[4] R. S. Mulliken, J. Chem. Phys. 3 (1935): XI, XII, the following articles.

bonding. The third solution, designated $[z_O+z_{CH_2}]$ in (1), probably is built mainly of $(2p_z)_O$ and $[z]_{CH_2}$ with the former probably more or less predominant, and probably gives fairly strong C−O bonding combined with some C−H bonding. A fourth solution, corresponding to an excited orbital which we shall encounter below under the designation $[z_{CH_2}-z_O, a_1]$, probably gives rather strong C−O antibonding and some C−H bonding (or possibly C−H antibonding). Very roughly, it seems likely, we may take $[z_O+z_{CH_2}]$ and $[z_{CH_2}-z_O]$ as solutions of a simpler perturbation problem starting from $(2p_z)_O$ and $[z]_{CH_2}$, thus isolating them from $(2s)_O$ and $[s]$. The foregoing statements in regard to the forms of the a_1 orbitals, while probably roughly correct, cannot be counted on as entirely reliable without more careful consideration.

For this reason, the estimated I's for these orbitals are less certain than for the others. The estimated I's given in (1) are based on the usual methods,[5] with $I^\circ=17.17$ volts, $I^*=14.73$ volts as $2p$ comparison I's of the O atom, and $I^\circ=11.21$ volts for $2p$ of the carbon atom. The estimated I for $[x_O+x_C]$ is obtained as follows:

$$I>\tfrac{1}{2}\{I^\circ(2p_O)+I^\circ(2p_C)\},$$

which gives $I>14.2$, say I about 17.5, since I should be at least as large as $I^\circ(2p_O)$. Allowance for the fact that the O atom has a considerable net negative charge reduces the estimate[5] to perhaps about 15.5 volts.

The predicted I for the nonbonding orbital $(2p_yb_2)_O$ is simply $I^*=14.73$ volts if no allowance is made for net charge on the O atom. If the charge on the O atom should prove to be about the same as in H_2O, as seems possible, although available electronegativity data[4] are not applicable here, we might expect the actual I to be reduced to about 12.7 volts as in H_2O, or lower (see below). Thus the minimum vertical I of H_2CO should without much doubt be the I for removal of a $(2p_y)_O$ electron.

The estimated I for $[yb_2]$ of the CH_2 radical is based on the idea that, as was likewise supposed for $[y]$ in C_2H_4, it is very similar to the y component of $[\pi]$ of the CH_3 radical in CH_3X or CH_4. The estimate given is somewhat larger than the $I=14.4$ volts of $[\pi]$ in CH_4, since the CH_2 group here is more positively charged because of the presence of the strongly negative O atom in the molecule. Interaction with $(2p_yb_2)_O$ should also tend to increase I of $[yb_2]$, I of $(2p_y)_O$ being decreased at the same time; but these effects are probably not large.

In a recent paper by Eastwood and Snow,[5a] dealing with the ultraviolet bands and electronic structures of aldehydes and ketones, the authors refer to an electron configuration given by the writer in 1933–4 letters to Dr. Snow. This differed from (1) above in that $[y+y]^2[y-y]^2$ was written instead of $[yb_2]^2(2p_yb_2)^2$; in other words, strong resonance between $[y]$ of CH_2 and $2p_y$ of O was assumed. This seemed necessary at the time, since the predicted I was about 14.4 volts for $[y]$ of CH_2 and 14.73 volts $=I^*(2p)$ for O. The writer was not quite satisfied with this conclusion in relation to the ultraviolet H_2CO bands, and publication was postponed. Price's recent work, leading to the realization of the importance of charge transfer effects,[5] also other evidence tending to indicate lack of strong resonance in certain analogous cases even in the presence of degeneracy,[5] cleared up the remaining doubts, and led to the present conclusion that there is not much interaction between $[y]$ of CH_2 and $(2p_y)$ of O, and that the latter has a considerably smaller I than the former, mainly because of charge-transfers. Nevertheless there must be *some* interaction and mixing between the two orbitals, possibly enough to affect their I's appreciably.

The observed I_{min} of H_2CO is 11.3 ± 0.5 volts according to Jewitt (electron impact method), and 10.83 ± 0.1 volts according to Price (Rydberg series).[6] Although these values are considerably lower than that suggested above, there is practically no doubt that they must be identified with removal of $(2p_y)_O$; strong evidence supporting this is obtained from certain ultraviolet bands to be discussed below. A reasonable explanation of the low I is as follows: in H_2O the nonbonding analog $(2p_z)_O$ of the present $(2p_y)_O$ is in the field of the net negative charge on the O, but this field is partly compensated by the fields of the

[5] R. S. Mulliken, J. Chem. Phys. **3**, 514 (1935): VIII.

[5a] E. Eastwood and C. P. Snow, Proc. Roy. Soc. **A149**, 434 (1935).

[6] T. N. Jewitt, Phys. Rev. **46**, 616 (1934); W. C. Price, Phys. Rev. **46**, 529 (1934), and private communication.

nearby positive charges on the H's. In H_2CO, assuming the same net negative charge on the O as in H_2O, the net lowering of I of $(2p_y)_O$ is greater because the corresponding positive charges, mostly on the H's but partly on the C, are now very considerably farther away. Possibly interaction with $[y]$ of CH_2 also has an appreciable part in making I low for $(2p_y)_O$.

2. Ultraviolet Bands of Formaldehyde and other Aldehydes and Ketones

Now we can proceed to the interpretation of the ultraviolet H_2CO bands near λ2900.[5a, 7, 8, 9] Of especial importance is the rotational analysis[9] of several of the bands by Dieke and Kistiakowsky. This shows that the molecule still has the plane Y shape in the upper electron level, and that the three moments of inertia are all increased by amounts ranging from about 8 to 15 percent. From this it follows that the H−H distance is increased, but that the C−O distance is increased more in proportion; what has happened to the C−H distances is not determined.

The rotational analysis shows that, for the six bands investigated, including A, B, C of the main vibrational series (λλ3520, 3390, 3260), the electric moment of the transition vibrates in the y direction, i.e., in the plane of the molecule. The selection-polarization rules[10] for symmetry C_{2v} permit a y electric moment only for transitions $A_1 \longleftrightarrow B_2$ or $A_2 \longleftrightarrow B_1$. (Note that for symmetry C_{2v} the x, y, z components of electric moment belong, respectively, to the representations b_1, b_2 and a_1.)[10]

Now it must be recognized that we cannot in general assume that a y electric moment necessarily means a $B_2 \longleftrightarrow A_1$ or $A_2 \longleftrightarrow B_1$ *electronic* transition. Instead, the symbols A_1, B_2, A_2, B_1 refer in general to the *total* $e\times v$ (*electronic* $\times$*vibrational*) state. Electronic, vibrational and total $e\times v$ state are all classified according to representations of the group C_{2v}, and the representation to which the total $e\times v$ state belongs is the direct product of the representations to which the electronic and vibrational states separately belong.[10] For example, if the electronic state is $^1B_2$ and the vibrational state is A_2, the total $e\times v$ state is $^1B_2\times A_2 = {}^1B_1$; similarly, $^1A_1\times A_1 = {}^1A$; $^1A_1\times B_1 = {}^1B_1$, $^1B_2\times A_1 = {}^1B_2$, $^1B_2\times B_1 = {}^1A_2$; $^3B_2 \times B_1 = {}^3A_2$; etc.[10]

In case we should know that the vibrational states involved are both totally symmetrical (i.e., type A_1), or at least both alike, for the upper and lower electron levels, *then* we could conclude from the observed y electric moment that the *electron* transition is either $A_1 \longleftrightarrow B_2$ or $B_1 \longleftrightarrow A_2$. There is, of course, no doubt that the lower electron level is of type $^1A_1$ (cf. Eq. (1)). Hence, if only symmetrical vibrations are present for the bands analyzed, the upper electron level is B_2, doubtless $^1B_2$ since transitions to $^3B_2$, if present, should be much weaker than to an accompanying $^1B_2$. We must now consider two possibilities: (*a*) the electron transition is one allowed by the electronic selection rules; (*b*) it is one forbidden by these rules. The second possibility is of course unlikely, but nevertheless cannot be entirely ruled out, since the selection rules are rigorous only for the total $e\times v$ state, and only approximately so for the electronic and vibrational states separately.[11]

If (*a*) the electronic transition is an allowed one, then we can confidently conclude that the transition is $^1A_1 \longleftrightarrow {}^1B_2$. For with an allowed electron transition, the strongest bands in the system, and all long series of strong bands, must conform to the Franck-Condon principle; now three of the bands analyzed belong to a long strong series which includes the strongest bands; and it can be seen that only symmetrical vibrations (type a_1, giving resultant vibrational states A_1) can be strongly excited without conflicting with the Franck-Condon principle.

We now seek to determine the electron configuration of the $^1B_2$ state indicated by the preceding discussion. Possible excited states which might have fairly low energy are

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[7] V. Henri and S. A. Schou, Zeits. f. Physik **49**, 774 (1928). G. Herzberg, Trans. Faraday Soc. **27**, 378 (1931). Vibrational analysis.

[8] G. Herzberg and K. Franz, Zeits. f. Physik **76**, 720 (1932); S. Gradstein, Zeits. f. physik. Chemie **B22**, 384 (1933). Fluorescence.

[9] G. H. Dieke and G. B. Kistiakowsky, Proc. Nat. Acad. Sci. **18**, 367 (1932); Phys. Rev. **45**, 4 (1934). Rotational analysis.

[10] R. S. Mulliken, Phys. Rev. **43**, 279 (1933): IV. Cf. Table I, noting with care the last paragraph of "Explanation of Tables," which is rather condensed, and section 5. Or cf. A. Bushkovitch, Phys. Rev. **45**, 545 (1934).

[11] G. Herzberg and E. Teller, Zeits. f. physik. Chemie **B21**, 410 (1933).

$$(2p_yb_2)^{-1}[x_C-x_O,\ b_1],\ ^{1,3}A_2;\ (2p_yb_2)^{-1}[z_{CH_2}-z_O,\ a_1],\ ^{1,3}B_2;$$
$$[x+x,\ b_1]^{-1}[x-x,\ b_1],\ ^{1,3}A_1;\ [x+x,\ b_1]^{-1}[z-z,\ a_1],\ ^{1,3}B_1;$$
$$[z+z,\ a_1]^{-1}[x-x,\ b_1],\ ^{1,3}B_1;\ [z+z,\ a_1]^{-1}[z-z,\ a_1],\ ^{1,3}A_1;$$
$$[yb_2]^{-1}[x-x,\ b_1],\ ^{1,3}A_2;\ [yb_2]^{-1}[z-z,\ a_1],\ ^{1,3}B_2; \qquad (2)$$

and another set of states like those in the second column except for the substitution of $3sa_1$ for $[z_{CH_2}-z_O,\ a_1]$. Since we are looking for a $^1B_2$ upper level, our attention centers on the states with configurations $(2p_yb_2)^{-1}[a_1]$ and $[yb_2]^{-1}[a_1]$, where $[a_1]$ may be $[z-z,\ a_1]$ or $3sa_1$. As between $[yb_2]^{-1}$ and $(2p_yb_2)^{-1}$, the first can safely be dismissed in favor of the second, in view of our study of predicted and observed I values. Granting this, we have only to decide between the two possibilities for $[a_1]$.

In the band system near λ2900, now under discussion, the first band starting from the vibrationless normal molecule (band A) has a frequency corresponding to 3.5 volts, while the peak of intensity (near band F) corresponds to 4.2 volts. The latter may be taken as the approximate *vertical* excitation energy for the electron transition. On subtracting it from 11 volts, the approximate vertical I of the molecule, identified above with removal of $(2p_yb_2)$, we get about 6.8 volts as vertical term value for $[a_1]$. This value is surely too large for $3sa_1$, whether the latter is centered near the O atom or between the O and C.

This leaves $^1B_2$ of

$$(2p_yb_2)^{-1}(z_{CH_2}-z_O,\ a_1),\ ^{1,3}B_2 \qquad (3)$$

as the probable upper level of the observed bands. An objection may be raised to this on the ground that in previous papers, especially IX,[2] the orbital $(z-z)$, e.g., in C_2H_2, C_2H_4 and C_2H_6, has been considered be to very high in energy, i.e., to have a term value even smaller than $3s$. In view of the strong polarity of the C−O bond here, however, $[z-z]$ here may well be very considerably different in term value than in more symmetrical molecules.

We come thus to the conclusion that, if the electron transition is an allowed one, there is little doubt that its upper level is $^1B_2$ of (3). It may be advisable, however, to consider the possibility that the electron transition is of forbidden type. The only possibility of this, since the normal state is surely $^1A_1$, is $^1A_1\rightarrow A_2$, doubtless $^1A_1\rightarrow{}^1A_2$. This is, however, possible only if the transition for the total $e\times v$ state obeys the rigorous selection rules; furthermore, to agree with observation, the transition must give a y electric moment and so be either $A_1\leftrightarrow B_2$ or $A_2\leftrightarrow B_1$. Two likely ways in which these conditions could be satisfied for the observed bands are

$$(^1A_1\times A_1=\ ^1A_1)\rightarrow(^1A_2\times B_1=\ ^1B_2) \qquad (4a)$$

or

$$(^1A_1\times B_1=\ ^1B_1)\rightarrow(^1A_2\times A_1=\ ^1A_2). \qquad (4b)$$

In (4a), we may start from a nonvibrating molecule and end with a molecule in a vibrational state B_1, which could be obtained most simply if one quantum of a mode of vibration of symmetry b_1 is excited, together with any number of quanta of symmetry a_1. In (4b), we start from a molecule having, in the simplest case, one quantum of b_1 type; (4b) would become more intense with rise in temperature. There is for H_2CO just one mode of vibration of symmetry b_1, namely, the mode in which the molecule bends out of its plane equilibrium form. This should have a very low frequency. Although its strong excitation, in (4a) especially, would be counter to the Franck-Condon principle, it seems quite possible that the necessary absorption (4a), or loss (4b), of one vibrational quantum of this mode might occur fairly readily.

As for the reason why a "forbidden" electronic transition could occur,[11] this can be explained as follows, taking (4a) as an example. The (4a) $e\times v$ levels of type $(^1A_2\times B_1=\ ^1B_2)$ may be perturbed by other $^1B_2$ $e\times v$ levels of the molecule, of type $^1B_2\times A_1=\ ^1B_2$, probably belonging to a higher-energy electron state. Since transitions to $(^1B_2\times A_1=\ ^1B_2)$ from the normal state $(^1A_1\times A_1=\ ^1A_1)$ are allowed by the electronic selection rules, transitions to $(^1A_2\times B_1=\ ^1B_2)$ will also occur weakly when the latter are perturbed by $(^1B_2\times A_1=\ ^1B_2)$. Some support is given to this sort of interpretation of the observed band system by the fact that it is much weaker than other systems further in the ultraviolet. In the deriva-

tives of H_2CO (aldehydes and ketones), the intensity ratio between the bands near λ2900 and the next system near λ1900 is about 1 : 300, according to a letter from Dr. C. P. Snow. This ratio is, however, really not so very large, and many other examples are known, in diatomic as well as polyatomic molecules, where long wavelength bands are very much weaker than shorter wavelength bands, even when there is no reason to believe that the electronic transition is barred by a selection rule. Hence the low intensity of the bands is not at all conclusive evidence of a forbidden electronic transition; if anything, the observed intensity is surprisingly high for such.

There is, however, one feature of the spectrum near λ3000, not yet mentioned, which tends to favor the idea of a forbidden electron transition. The absorption spectrum contains a very weak band, called α, which does not fit in well with the others. It apparently comes from an excited vibrational state of the normal molecule, since it is reported[9] to be especially sensitive to temperature. Thus its weakness is partly explained, but there are other difficulties. Fluorescence can be excited in H_2CO by absorption of bands in the main system,[8] but apparently the actual fluorescence bands all start only from the upper level of α. It has been suggested[8] that the latter must be lower than the upper levels of any of the main bands, so that by collisions all molecules in higher levels are driven down to it before giving fluorescent radiation. In this case the upper level of α either must belong to a different electron state than for the other bands, or else the lowest upper vibrational state involved in the other bands is not one with all vibrational quantum numbers zero. The latter possibility could be understood if the lowest upper level observed in the other bands is of type $({}^1A_2\times A_1={}^1A_2)$. Transition to the latter from the normal, nonvibrating $({}^1A_1\times A_1={}^1A_1)$ state of the molecule would be rigorously forbidden, which would explain the fact that the upper level of band α can be reached only through absorption by already vibrating molecules (presumably of type $({}^1A_1\times B_1={}^1B_1)$, cf. (4*b*)).

The foregoing explanation would make α belong, with the other bands, to a forbidden electronic transition, with a ${}^1A_2$ upper electron level. If this is correct, there is for it one and only one acceptable electron configuration (cf. the possibilities in (2)), and this one entirely reasonable, namely

$$(2p_y b_2)^{-1}[x_C - x_O, b_1],\ {}^{1,3}A_2. \qquad (5)$$

This would make $[x-x]$ instead of $[z-z]$ the lowest excited orbital in H_2CO, which is reasonable and in accord with conclusions[2] in regard to C_2H_4 and O_2.

If the foregoing explanation of the α band, making the electron transition of forbidden type, is not correct, then it is probable that the α band has a different upper electron level than the other bands. This might possibly be ${}^3B_2$ of (3), but the temperature behavior of α and other evidence indicate that, if the other bands belong to an allowed electron transition, then α must belong to a forbidden one, probably that just suggested above for it. This would explain its *weakness;* its *presence* could be explained as a result of perturbation of its upper level $({}^1A_2\times A_1={}^1A_2)$ by levels of type $({}^1B_2\times B_1={}^1A_2)$ associated with the upper electron level of the other bands. If α belongs to a forbidden transition, the same reasoning used above leads clearly to ${}^1A_2$ of (5) as its upper electron level. In this case, we would have evidence of two excited electron levels, with ${}^1A_2$ of (5) a few tenths volt below ${}^1B_2$ of (3), and with $[x-x]$ slightly higher in I than $[z-z]$. The corresponding levels ${}^3A_2$ and ${}^3B_2$ would necessarily also exist, but bands to them would be very weak.

It will be noted that regardless of whether (3) or (5), or both, are the upper levels of the observed bands, our conclusion that $(2p_y)_O$ is the most easily ionized orbital in (1) receives confirmation, the possibilities $[x+x]$ and $[z+z]$ being directly ruled out by the y character of the electric moment, while $[yb_2]$ has been eliminated by other considerations. Thus we can conclude rather definitely that the electron transition involved in the bands is of the type

$$(2p_y)_O \rightarrow [a-a],$$

where $[a-a]$ is a C⟷O antibonding orbital, either $[z_{CH_2}-z_O]$ (probably) or $[x_C-x_O]$ (possibly).

This conclusion is in harmony with the effects of the transition on the moments of inertia.[9] These indicate, as noted above, that the C−O

distance is moderately increased, and that small or at most moderate changes occur in the HCH angle and CH distances. It also explains how, and in what sense, the transition is localized in the C=O bond; and it makes clear why an analogous band system, in very nearly the same wavelength region in all, is found in other saturated aldehydes RHCO and ketones RR′CO.

It may be helpful here to give electron configurations for CH_3HCO as a typical aldehyde and $(CH_3)_2CO$ as a typical ketone. For acetaldehyde we have, omitting $1s$ electrons:

$$(2s)^2[s]^2\ [s]^2\ [x+x]^2[y]^2[z+z]^2[\pi]^4(2p_y)_O{}^2,\ {}^1A. \qquad (6)$$
$$\text{O}\ \ CH_3\ HCCO\ \ CO\ \ HCC\ HCCO\ CH_3\ \ O$$

This is essentially the same as (1) except that the electrons $[s]^2[\pi]^4$ of the CH_3 group have been added, and except that in $[y]$, $[z+z]$, and the second $[s]$, the C of CO is bonded to one H and one C instead of to two H's as in H_2CO. No representation symbols have been used in (6), since strictly speaking there is no symmetry except for special and probably unimportant angles of rotation of the CH_3 group. Strictly speaking there is more or less interaction and mixing among all the various orbitals given in (6), also a splitting of $[\pi]$. Also there is some arbitrariness in using the CH_3 intraradical orbitals $[s]$ and $[\pi]$.

Nevertheless there are sufficient reasons for believing that the set of partially localized orbitals used in (6) constitutes a good approximation, corresponding well to observable I's with approximately correct localization of the "hole" in the electron density distribution produced by each I. (Cf. discussions in VII of this series[1] for further explanation.) Empirically, the similarity of the longer wavelength bands of H_2CO and CH_3HCO is satisfactory evidence that the orbitals involved in the C−O bond are nearly alike in H_2CO and CH_3HCO, so that (6) is a good approximation if (1) is. Farther in the ultraviolet, CH_3HCO should have bands and I's not found in H_2CO, namely, those corresponding to excitation of an electron from $[s]$ or $[\pi]$ of CH_3. The I's for these can be predicted to be approximately the same as for $[s]$ and $[\pi]$ of CH_3 in CH_4 or CH_3I. In practice, the spectrum of I's and of bands will tend to become perhaps hopelessly complicated at shorter wavelengths.

For $(CH_3)_2CO$ a configuration similar to (6) can be written, but with an $[s]$ and $[\pi]$ group for *each* CH_3. The observed I, as recently obtained by Noyes and Duncan[11a] (10.20 volts from a probable Rydberg series, 10.1 volts from electron impact), is remarkably low, but must again be ascribed to $(2p_y)_O$.

In a recent paper,[5a] Eastwood and Snow have studied the changes in the longest wavelength bands in going from H_2CO to other aldehydes. On this basis they adduce empirical evidence (change of C−O vibration frequency of the upper electron level) which tends to favor $(2p_y)_O \rightarrow [z-z]$ as against $(2p_y)_O \rightarrow [x-x]$ for the electron transition involved. This evidence indicates lack of complete localization of the transition in the C−O bond, in agreement with $(2p_y)_O \rightarrow [z-z]$.

In the shorter wavelength ends of the λ2900 band of H_2CO[7] and of analogous bands of the other aldehydes and ketones, marked predissociation occurs. The fact, demonstrated by Norrish,[12] that the predissociation in H_2CO gives H_2+CO, in RHCO gives RH+CO, and in RR′CO gives RR′+CO (R = alkyl or substituted alkyl radical), has in the writer's opinion little, if any, direct dependence or bearing on the nature of the electron transition involved. The writer's view would be that the excited and vibrating molecule in each case simply predissociates into another electronic state whose n-dimensional potential energy surface is such that the molecule breaks up directly into CO plus H_2 or RH or RR′. There seems to be no need that the primary excitation process shall have any special loosening effect on the C−H or C−R bonds, as apparently it does not.

The absence or at least extreme slowness of predissociation from the upper level of the α band in H_2CO, shown by its ability to serve as upper level for fluorescence,[8] may be taken as evidence, although not conclusive, that the α band belongs to a different electron transition than the other bands.

[11a] A. B. F. Duncan, J. Chem. Phys. **3**, 131 (1935); W. A. Noyes, Jr., J. Chem. Phys. **3**, 430 (1935).

[12] R. W. G. Norrish and co-workers. cf. Trans. Faraday Soc. **30**, 108 (1934).

In concluding this section, we should mention the second ultraviolet system found in aldehydes and ketones, and attributed, like the first system, to a transition in the C=O bond (cf. beginning of this paper). A number of possibilities for the upper state of these bands are included in (2) and in (2) modified by substituting $3sa_1$ for $[z-z, a_1]$. Transitions from the normal state to any of these, with the exception of those involving $[yb_2]^{-1}$, are localized more or less completely in the C=O bond, and so would be capable of accounting for the occurrence of the bands in question with little modification in all aldehydes and ketones. The possibilities are so numerous, however, that it would be futile, without further knowledge of the band structure, to attempt to decide which one or ones correspond to the actual bands. (The fact[12] that absorption in this region does not cause predissociation to give CO seems to be of no particular help here.) Transitions from the normal state to all types except A_2 are allowed by the electronic selection rules, with electric moments x, y, z, respectively, for upper electron levels B_1, B_2 and A_1. It is probable, however, that many of the allowed transitions are very weak or are represented by continua rather than discrete bands.

3. Other Molecules Containing C=O and C=S Bonds

The characteristic absorption bands of the C=O bond as found in aldehydes and ketones may reasonably be expected to occur also in other compounds of the general type $\begin{matrix}A\\B\end{matrix}\!\!>\!C=O$, while analogous bands are to be anticipated in $\begin{matrix}A\\B\end{matrix}\!\!>\!C=S$. Cases like O=C=O, O=C=S, S=C=S, etc., where the symmetry is quite different, should not be expected to show bands corresponding in any close way to those of the C=O and C=S bonds in ABC=O and ABC=S; they will be considered in XIV of this series.

In cases like $R-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-R$ with two C=O bonds close together, the beginning of absorption is observed to be displaced toward longer wavelengths. This is apparently a result of some kind of strong interaction within the O=C−C=O system of bonds. These and other similar cases[12a] will, however, not be considered in this paper.

A few examples of the types ABC=O and ABC=S will now be taken up. In the important molecule phosgene, $O=CCl_2$, which has symmetry C_{2v} just like H_2CO, the two H atoms of H_2CO are replaced by Cl atoms. The electron configuration should be qualitatively the same as (1), except for the addition of Cl nonbonding electrons. Omitting inner electrons, the configuration should be

$$\underset{O}{(2s)^2}\underset{Cl}{(2s)^2}\underset{Cl}{(2s)^2}\underset{Cl_2CO}{[sa_1]^2}\underset{O-C}{[x_O+x_C,\ b_1]^2}\underset{CCl_2}{[yb_2]^2}\underset{O-CCl_2}{[z_O+z_{CCl_2},\ a_1]^2}\underset{Cl}{(3p\pi)^{2\times2}}\underset{Cl}{(3p\pi)^{2\times2}}\underset{O}{(2p_yb_2)^2},\ {}^1A_1. \qquad (7)$$

The $3p\pi$'s of Cl are really each slightly split into an xb_1 and a yb_2 component, and in addition there should be resonance between the two resulting xb_1's, and between the two yb_2's. However, these splittings are doubtless not large, and will be neglected here.

In (7), it is doubtful whether the minimum I is that of $3p\pi_{Cl}$, or of $(2p_y)_O$ as in CH_2O. We know that I is 11.2 volts for $3p\pi_{Cl}$ in CH_3Cl, while I is 10.9 volts for $(2p_y)_O$ in CH_2O. It is probable that both I's are somewhat larger in $COCl_2$. Since O and Cl are competing for negative charge, the net negative charge on Cl is probably appreciably less than in CH_3Cl, and that on O less than in H_2CO. Hence the I's should be somewhat greater.[5]

We expect that the spectrum of $COCl_2$ should contain a band system analogous to that in COH_2 near λ2900, i.e., of the type $(2p_y)_O \rightarrow [z_O - z_{CCl_2}]$ or $[x_O - x_C]$. If I is somewhat greater here for $(2p_y)_O$ than in H_2CO, and if the term value for $[z-z]$ or $[x-x]$ is nearly the same as in H_2CO, as would be expected, then these $COCl_2$ bands should be at somewhat shorter wavelengths than the corresponding bands in H_2CO. Actually the $COCl_2$ spectrum does begin at somewhat shorter

[12a] E. Eastwood and C. P. Snow, Proc. Roy. Soc. **A149**, 446 (1935).

wavelengths than that of COH_2, and resembles the latter.[13] The spectra of $(CH_3)ClCO$, (CH_2Cl)-$ClCO$, $(CCl_3)ClCO$, $(CBr_3)HCO$ are also found to be similar,[14] as might be expected; $(CCl_3)HCO$, strangely, seems to be somewhat different.

If I is nearly the same for $3p\pi_{Cl}$ as for $(2p_y)_O$ in $COCl_2$ and similar compounds, we should be inclined to expect transitions $(3p\pi_{Cl})\rightarrow X$, with absorption wavelengths near those of the transitions $(2p_y)_O\rightarrow[z-z]$ or $[x-x]$. Possibly the observed absorption near λ2500 in these compounds,—or part of it,—is of this type.

Now suppose an S atom is substituted for the O atom in (1) or (7). There should be no formal changes in the electron configuration, only that S replaces O everywhere, and in particular, that $(3s)_S$ and $(3p_yb_2)_S$ replace $(2s)_O$ and $(2p_yb_2)_O$. An important change is that the polarities of the C−S bonding orbitals should be reduced in H_2CS and Cl_2CS, as compared with those of the corresponding C−O orbitals in H_2CO and Cl_2CO, since C and S are nearly equal in electronegativity, at least for C−S single bonds according to Pauling's scale.[4] This equality, however, may be less nearly true for C=S.

Of most interest for our purpose is I for the molecule, and its relation to the position of observed bands. The predicted I for $(3p_y)_S$ is $I^*=10.83$ volts,[5] as compared with $I^*=14.73$ volts for $(2p_y)_O$. The observed I for $(2p_y)_O$, as noted above, is about 10.9 volts in H_2CO, or 3.8 volts less than the predicted; this was accounted for by accumulation of negative charge on the O atom. For $(3p_y)_S$ in $\rangle C=S$ we would expect the difference between I_{obs} and I^* to be notably smaller than in corresponding $\rangle C=O$ compounds, since the net negative charge on the S must be less than on the O, possibly nearly zero.

Actually, we have no I data on compounds $\rangle C=S$, but a comparison may be made between *spectra* of these and $\rangle C=O$. In particular, data are available for Cl_2CO and Cl_2CS.[13, 15] The first absorption region in Cl_2CO begins at about λ3042, and reaches its intensity maximum at about λ2500 (?). The first region in Cl_2CS begins at about λ5712 and reaches a maximum at about λ4800 (?); it is relatively weak. It appears fairly safe to assume that this first region of absorption in Cl_2CS is entirely analogous to that in Cl_2CO and other molecules $\rangle C=O$ and $\rangle C=S$. That is, it probably corresponds to a transition

$$(3p_y)_S\rightarrow[z_C-z_{SCl_2}] \text{ or possibly } [x_C-x_S]. \quad (8)$$

If we neglect the change in I for the *excited* orbital, which is probably not great, then the shift in frequency of the first absorption region from Cl_2CO to Cl_2CS may be taken as a rough measure of the charge in I from $(2p_y)_O$ to $(3p_y)_S$. From the rough wavelength data given above the shift is roughly about 2.4 volts, hence if I is about 11.5 volts (a reasonable estimate) for $(2p_y)_O$ in $OCCl_2$, then it is probably about $(11.5-2.4)=9.1$ volts for $(3p_y)_S$ in $SCCl_2$. This value being considerably less than the calculated $I=10.83$ volts for $3p_S$, it appears that there must be still a considerable net negative charge on the S in $SCCl_2$, although by no means as much as on the O in $OCCl_2$.

Although the indicated considerable negative charge on the S here is rather surprising, the results are qualitatively as expected, and it appears very probable that the transition (8) in the C=S group is the cause of the color[15] possessed by many compounds of the type $S=C\langle$.

Next we may consider molecules of the types $O=C\langle^{R}_{OH}$ and $O=C\langle^{R}_{OR'}$, also $O=C\langle^{OR}_{OR'}$ (organic acids and esters). In such cases one might expect to find absorption band systems corresponding to the electron transitions within the C=O group, exactly like those in the aldehydes and ketones, except that in the acids RCOOH, there is a modifying influence in the

[13] V. Henri, *Structure des Molecules* (Paris, 1925). Cf. especially pp. 88–92, and the plates.

[14] R. A. Rehman, R. Samuel and Sarf-ud-Din, Ind. J. Phys. **8**, 537 (1934).

[15] Purvis, Jones and Tasker, J. Chem. Soc. (London) 110, 520 (1924). Absorption spectra of $SCCl_2$, $SC(OR)_2$, $SC(OR)(SR)$, $SC(SR)_2$, $OC(OR)_2$, $OC(OR)(SR)$, $OC(SR)_2$ etc. in dilute ethyl alcohol solutions. $SCCl_2$ is reported to be an orange-red liquid. In all these cases, the absorption is reported to begin in the ultraviolet. Apparently the solutions were too dilute for the detection of the comparatively weak visible absorption system of the $\rangle C=S$ types; found[13] by Henri in $CSCl_2$, and whose presence must be responsible for the colors reported for some of these substances.

fact that the H atom may be labile and tend to jump from one O atom to the other, or to locate itself between them. These expectations seem to be confirmed by the experimental evidence, but a detailed consideration will not be undertaken here.

Similarly, molecules like

$$S=C\begin{matrix}R\\OR'\end{matrix}, \quad S=C\begin{matrix}OR\\OR'\end{matrix}$$

etc., should have characteristic S=C absorption[15] like that in $S=CCl_2$. The same is true of molecules like

$$S=C\begin{matrix}OR\\SR'\end{matrix}, \quad S=C\begin{matrix}SR\\SR''\end{matrix}, \quad S=C\begin{matrix}R\\SR\end{matrix}$$

etc.[15] In all these cases, the molecule must *also* be regarded as a derivative of H_2O or H_2S, and there should be absorption regions, but at shorter wavelengths than the first absorption region of the C=O or C=S, associated with excitation of np nonbonding electrons of the single-bonded O or S atoms.[1] It is interesting to note that, although the most easily excited electron in both $\rangle C=O$ and $\rangle O$ is found to be a nonbonding $2p$ electron of the O atom, excitation is easier in the former case, partly because I is lower there for the nonbonding electron, and partly because I is higher for the lowest available excited orbital there. Analogous statements hold, of course, for the S compounds.

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Electronic Structures of Molecules

XI. Electroaffinity, Molecular Orbitals and Dipole Moments

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A convenient criterion for defining equal electronegativity of two atoms is stated in terms of coefficients in LCAO approximate molecular orbitals. Connections between relative electronegativities, coefficients in LCAO orbitals, effective charges on atoms in partially polar molecules, and dipole moments, are then analyzed, and various equations are obtained expressing these connections. The discussion is largely applicable to polyatomic as well as to diatomic molecules. A theoretical derivation is given for an empirical equation, found by Pauling, which forms a basis for the latter's approximate scale of relative electronegativities. Pauling's and other possible approximate scales are discussed, and it is shown how an approximate "absolute electroaffinity" can conveniently be defined on each scale. A very rough theoretical justification is given for the empirically observed proportionality between relative electronegativities obtained from Pauling's and from the writer's scale. The necessary existence of a "homopolar dipole" contribution to the electric moment of any bond is shown, provided the atoms forming the bond are of unequal size. By "homopolar dipole" is meant a contribution which would not vanish, for atoms of unequal size, even if they are of equal electroaffinity. Dipole moments of H_2O, NH_3 and HX are briefly discussed. It is concluded that the dipole moment scale of electronegativity is probably not well founded. An important object of the paper is to show how electroaffinity and other data can be used in the approximate determination of the polarities of molecular orbitals and so of bonds, the results being expressed both in terms of coefficients in LCAO molecular orbitals and in terms of effective charges transferred. Applications are made to the electronic structures of various diatomic molecules, especially HI, HI^+, HO^-, ClO^-.

1. INTRODUCTION

IN determining the electron configurations of molecules, we may proceed semi-empirically by considering alternative possibilities based on rough theoretical schemes, and then making choices in harmony with empirical data. The most convenient simple and generally applicable way of working out such theoretical schemes with molecular orbitals is to use LCAO approximations for the latter, at least for the normal and some of the low excited states. By using these in connection with certain semi-empirical rules it is possible even to make approximate predictions of I's (ionization potentials) for the real (Hartree-

field) orbitals to which the LCAO forms[1] are approximations.

To a considerable extent, the vital coefficients which appear in an LCAO form, i.e., the coefficients of the atomic orbitals used, are determined by symmetry considerations (cf. IV, V of this series[2, 3]). Even when rigorous symmetry is lost the existence of an approximate symmetry is often sufficient to guarantee that the coefficients are nearly the same as for a related case with exact symmetry. Another important principle similar to the foregoing is that,—even aside from symmetry considerations,—if the approximate form and energy of an orbital are known in one molecule, then these may be expected to be approximately preserved in many cases in other related (e.g., "derivative") molecules. A necessary condition for this preservation is of course that the field of force in the region of the orbital in question shall be nearly the same in the parent and derivative molecules (for examples, cf. VII, IX, and others of this series).[4]

The coefficients in LCAO forms depend in an important way, however, not only on symmetries of molecules and their parts, but also on the polarities of the bonds. This fact has been used in earlier papers in a rough qualitative way. The present paper is devoted primarily to a more careful consideration of the effects of polarity on LCAO coefficients, so that our knowledge of the LCAO forms and thereby our understanding of the real molecular orbitals may be made more precise.

It will be shown that electronegativity scales[5, 6] can in many cases be made use of qualitatively and even semi-quantitatively in determining how the LCAO coefficients are affected by polarities of bonds. It should be mentioned, however, that the existing scales have a meaning only in the cases of neutral molecules with electron-pair bonds and not too strongly polar. For strongly polar or heteropolar molecules, and for molecule-ions, the same qualitative principles can still be applied as in the less polar cases, but the values of LCAO coefficients must be estimated in other ways than by the electroaffinity scales hitherto proposed.

2. A New Basis for the Electroaffinity Scale for the Case of Neutral Uniunivalent Diatomic Molecules

In papers where electronegativity scales have been set up,[5, 6] the discussion has been given wholly in terms of atomic oribtal approximations for molecular electronic structures. It is equally possible, in fact simpler, to set up an electroaffinity scale in terms of molecular orbital approximations, at least if we use LCAO forms for the latter.

It is best to begin with neutral uniunivalent diatomic molecules. Suppose we have a bonding molecular orbital (ordinarily occupied by two electrons) approximated by the LCAO form

$$\phi_{AB}=a^{\times}\phi_A+b^{\times}\phi_B. \qquad (1)$$

If $a^{\times}=b^{\times}$, or $a^{\times 2}=b^{\times 2}$, we may say that the atoms A and B are of equal electroaffinity or electronegativity; or if $a^{\times 2}>b^{\times 2}$, that A is the more electronegative. Conversely, if we know the relative electroaffinities of two atoms, we can determine whether $a^{\times 2}>b^{\times 2}$ or $b^{\times 2}>a^{\times 2}$. Either $a^{\times}=b^{\times}$ or $a^{\times 2}=b^{\times 2}$ may be taken as a criterion of equal electroaffinity, but it will be shown below that, when we consider differences in electroaffinity, these can be more simply related to $a^{\times 2}-b^{\times 2}$ than to $a^{\times}-b^{\times}$ (cf. Eqs. (21), (22)).

The criterion of equal electroaffinity just set up is ordinarily nearly but not exactly equivalent to the criterion[6] $\alpha=\beta$ based on atomic orbitals. As a matter of fact it is probably inherently impossible to define equality of electronegativity other than approximately, except for $A\equiv B$.

The use of (1) with $a^{\times}=b^{\times}$ or $a^{\times 2}=b^{\times 2}$ implies, as one sees from perturbation theory, an effective equality of term values, i.e., an effective degeneracy, between the atomic orbitals ϕ_A and ϕ_B. In other words, equal electronegativity of two atoms A and B implies effective degeneracy between their respective valence orbitals.

As can be seen, however, from work of Hund,[7]

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[1] R. S. Mulliken, J. Chem. Phys. **3**, 375, 514 (1935): VI, VIII of this series.
[2] R. S. Mulliken, Phys. Rev. **43**, 279 (1933): IV.
[3] R. S. Mulliken, J. Chem. Phys. **1**, 492 (1933): V.
[4] R. S. Mulliken, J. Chem. Phys. **3**, 506, 517 (1935): VII, IX.
[5] L. Pauling, J. Am. Chem. Soc. **54**, 3570 (1932); L. Pauling and D. M. Yost, Proc. Nat. Acad. Sci. **18**, 414 (1932).
[6] R. S. Mulliken, J. Chem. Phys. **2**, 782 (1934).
[7] F. Hund, Zeits. f. Physik **73**, 1 (1931): especially pp. 18–19, 25–26.

the effective degeneracy for $a^\times = b^\times$ is not in general between the orbitals ϕ_A and ϕ_B as they exist in the free neutral atoms A and B. The case of H_2 illustrates the point. In constructing an LCAO bonding orbital for H_2, one of the two electrons is thought of as replaced by a continuous charge distribution, of which half (i.e., a charge $-\frac{1}{2}e$) is near each nucleus. This gives the Hartree field whose Schrödinger equation is to be solved for the molecular orbital. As the distance r between the nuclei goes to infinity this field becomes that of two centers each with a net charge $+\frac{1}{2}e$. The mean effective charge is, however, somewhat greater, say Z^*e, because the second electron penetrates the region occupied by the first.

The LCAO approximation (1) is obtained by, so to speak, taking r out to infinity and then back again. If we follow the real molecular orbital of the above-defined Hartree field to $r=\infty$, it is seen there to take on the form $2^{-\frac{1}{2}}(\phi_A+\phi_B)$, where ϕ_A and ϕ_B are $1s$ atomic orbitals, although not of ordinary H atoms ($Z=1$) but of certain central fields (*roughly* Coulomb fields with $Z_{eff}=Z^*$). If now we return from $r=\infty$ to the actual r, i.e., r_e, it will be seen that the form $a(\phi_A+\phi_B)$ should still serve as a more or less good zeroth approximation (LCAO approximation) to the actual molecular orbital. The error involved in the LCAO form, or at any rate in the energy, is considerably reduced by now using orbitals corresponding to a revised value of Z^* (obtainable, e.g., by a variation method) rather than to the value of Z^* which would be appropriate for $r=\infty$. In the case of H_2, for instance, Hund finds the best such Z^* to be about 0.85.[7] Now when two electrons are assigned to such an LCAO orbital, a basis is obtained for a tolerable approximation to the actual H_2 normal state wave function, provided r is not allowed to be large. For large r the approximation becomes very poor (regardless of Z^*) because of overionicness,[1] since really as $r\to\infty$ the molecule dissociates into two neutral atoms.

If A and B are two different univalent atoms, their orbitals ϕ_A and ϕ_B in ϕ_{AB} of (1) correspond to two different Z^*'s, i.e., Z^*_A and Z^*_B. As in the case of H_2, each of these should be somewhat less than the corresponding Z^n, where Z^n is the effective Z of the orbital ϕ for the neutral atom ($Z^n=Z=1$ for H, but for other atoms $Z>Z^n>1$). Of more interest than the Z^*'s, however, are the corresponding term values, since if these are equal we have effective degeneracy and equal electroaffinity of ϕ_A and ϕ_B.

Here we can be guided by Hund's calculation[7] on H_2, where the term values of ϕ_A and ϕ_B corresponding to the best Z^*, giving an energy for H_2 agreeing with experiment, were found to be a little less than $(I_H+E_H)/2$, where E=electron affinity. Generalizing from this example, it seems likely that in any molecule AB which is not too strongly heteropolar, the desired LCAO term value of, e.g., ϕ_A may be fairly well approximated by $(I_A+E_A)/2$, or at least be *proportional* to the latter, which is all that is needed for our purpose. This suggests that a quantity proportional to $(I+E)/2$ may be taken as a more or less good measure of the "absolute electroaffinity" of an atom, as was proposed in a previous paper[6] on the basis of an even rougher argument than that given here. The argument is of course still merely one of plausibility, the real justification for the use of $(I+E)/2$ remaining essentially empirical.[6] Nevertheless it shows that the appearance of $(I+E)/2$ as electroaffinity is reasonable.

The foregoing considerations will be refined by a more careful treatment below, especially in section 6. In connection with the use of the quantity $(I+E)/2$, it should be recalled[6] that it is necessary to take I and E values not for the ordinary normal state of atom and ion, but in general for suitable "valence states."

The discussion given in the next-to-last paragraph is in one respect not quite adequate. On going back, it will be noted that we are dealing with a pair of equivalent bonding electrons, each of which in turn may be used to produce a Hartree field for the other. Now if say $a^\times > b^\times$ for the resulting orbital (atom A more electronegative than B), then the basis of the Hartree field must be a charge distribution having more negative charge near atom A than near B. [Incidentally, it is not advisable to worry about how this charge distribution would actually change as $r\to\infty$, if allowed to adjust itself continuously. The best LCAO form here is one based on a partition of charge between A and B which corresponds to the situation for the actual small value of r, but which would have no real significance for $r=\infty$.]

The polarity of the Hartree field produced by the first electron thus makes the net positive charge less than $\frac{1}{2}e$ on atom A and greater than $\frac{1}{2}e$ on atom B, i.e., it diminishes Z^* for the former and increases it for the latter, as compared with the homopolar case. Thus it decreases the effective difference in electronegativity between the two atoms, and makes the orbital ϕ_{AB} less polar than one might at first have anticipated. It can be shown, however (see near end of section 6) that the difference in electronegativity, i.e., in effective term values, between A and B remains approximately *proportional* to what it would be without allowance for the transfer of charge from A to B. Thus the occurrence of charge transfer does not affect the validity of the argument given above indicating that the difference in electronegativity is approximately proportional to the difference between the quantities $(I+E)/2$ of the neutral atoms A and B.

3. Diatomic Molecular Ions

Let us next consider positively charged molecules in which there is only one bonding electron (examples: H_2^+, Li_2^+, $(LiK)^+$, $(HI)^+$). In such cases the LCAO approximation remains valid, in fact becomes *increasingly good*, as $r\to\infty$. Here $Z^*=Z^n$ for each atom ($=1$ for H), at least for $r=\infty$, hence the quantity I rather than $(I+E)/2$ is a proper measure of electroaffinity; a correction ought to be made, however, if possible, to get effective I's appropriate to $r=r_e$ instead of to $r=\infty$. Valence state rather than ordinary I's should of course be used. Other things being equal, the polarity of a given molecular orbital when occupied by only one electron should be greater than when occupied by two, since the mutual polarity-shielding effect discussed above in section 2 is absent.

An interesting application of the foregoing is to the bonding orbital of HI. The electron configuration,[8] omitting inner electrons, is

$$(5p\sigma_I+1s_H,\sigma)^2(5p\pi_I)^4,\ ^1\Sigma^+. \qquad (2)$$

Here $(5p\sigma_I+1s_H)$ represents the bonding orbital, given in LCAO approximation by

$$a(5p\sigma_I)+b(1s_H). \qquad (3)$$

In neutral HI, this has a pronounced H^+I^- polarity ($a>b$), corresponding to the fact that $(I+E)$ is greater for I than for H, if the proper valence states of I^+, I, and I^- are used in computing $(I+E)$ for I.[8, 6]

In the $(HI)^+$ state

$$(1s_H+5p\sigma_I,\sigma)(5p\pi_I)^4,\ ^2\Sigma^+, \qquad (4)$$

however, with only one bonding electron, the polarity of the bonding orbital may be mildly reversed (H^-I^+, $a<b$), since the valence I is somewhat less for I than for H (about 12.93 for I as compared with 13.53 volts for H; the value 12.93 is the $V_1\to V_0$ valence I, which is considerably larger than the ordinary I[8, 6]). This reversal of polarity is not certain, however, since the relative values of the effective I's might perhaps be reversed at $r=r_e$ as compared with $r=\infty$.

As another example, we may consider LiH and $(LiH)^+$. For neutral LiH, there is evidence that the molecule is a little nearer to the homopolar than to the ionic ideal case: the bonding orbital $a(1s_H)+b(2s_{Li})$ may have a/b perhaps about 2. The molecule is too strongly polar to permit use of the electroaffinity scale in more than a qualitative way; it may be noted that $(I+E)/2$ has the respective values 7.12 and about 2.86 for H and Li.

For $(LiH)^+$, we have to consider the I values 13.53 for H and 5.37 for Li. These tend to indicate a much greater polarity of the bonding orbital, and of the molecule, than in neutral LiH. It seems possible that the polarity of the orbital may even be so great (i.e., $a^\times$ nearly 1, $b^\times$ nearly 0) that the orbital becomes practically nonbonding, the molecule being then simply an atom-pair $H+Li^+$. There would also be an excited state with $a^\times$ then nearly 0, $b^\times$ nearly 1 (cf. Eqs. (7) below) of type H^++Li. Pauling[9] considers that $(LiH)^+$ and other molecules $(AB)^+$ containing a single bonding electron, unlike the corresponding neutral molecules with an electron pair, are unstable unless the term values of ϕ_A and ϕ_B are "essentially" equal, i.e., differ by less than the amount of the resonance energy. However, it would appear that the polarization energy should be comparatively large in most such cases and so should often suffice to give at least a modicum of stability, and make $b^\times$ appreciably larger than zero. Equations whereby the

[8] R. S. Mulliken, Phys. Rev. **46**, 549 (1934).

[9] L. Pauling, J. Am. Chem. Soc. **53**, 3225 (1931).

energy and coefficients can be approximately calculated for molecules $(AB)^+$ with one bonding electron are given below (Eqs. (7)–(11) and (16)–(17)).

Quite different is the case of positively charged molecules in which the bonding electron pair is left intact, but a nonbonding electron has been removed. As an example we may consider $(HI)^+$ in the (normal) state

$$(5p\sigma_I+1s_H,\ \sigma)^2(5p\pi_I)^3,\ ^2\Pi_{1\frac{1}{2}},\ \tfrac{1}{2}. \tag{5}$$

Since the electron which has been removed comes from the I atom, the primary effect on the bonding orbital should be to increase Z^* for $5p\sigma_I$. The H^+I^- polarity ($a^\times > b^\times$) of the bonding orbital should thus be increased as compared with the same orbital in neutral HI.

In seeking to determine the degree of polarity of the bonding orbital in (5) a comparison of the $(I+E)/2$ values for I^+ and H, it can be shown, is not appropriate. A helpful method here is to approximate the wave function of (5) using entirely atomic orbitals, and then to compare with (5). In terms of atomic orbitals, (5) corresponds essentially to the $^2\Pi$ of $H(1s)\cdot I^+(p\sigma p\pi^3, V_2)$ with only a little admixture of the $^2\Pi$ of $H^+\cdot I(p\sigma^2 p\pi^3, V_1)$; V_1 and V_2 are valence states.[6] The conclusion that $H^+\cdot I$ is relatively unimportant here is reached in view of the fact that the energy of $H(1s)+I^+(V_2)$ at $r=\infty$ is about 2.37 volts lower[6] than that of $H^+ + I(V_1)$, noting also that according to HLPS (Heitler-London-Pauling-Slater) theory the binding energy should be greater in the former case. For values of r corresponding to the stable molecule there should be only a small or moderate perturbation between the wave functions of the $U(r)$ curves of these two states. Hence the $^2\Pi$ normal state of HI^+ is mainly $H\cdot I^+(V_2)$, and we conclude that the polarity of the bonding orbital after all cannot be much greater than in neutral HI.

Similar methods can be applied in other cases where a nonbonding electron has been removed or excited: examples, $(5p\pi_I)^{-1}$ in $(ICl)^+$; $(3p\pi_{Cl})^{-1}$ in $(ICl)^+$. In I_2^+, of course, the bonding orbital remains homopolar, since the charge is shared equally by (or rapidly "resonates between") the two I's.

Negatively charged ions can be treated in similar ways; let us consider HO^- and ClO^- as examples. (CN^- is similar, but the presence of more than one bonding electron pair complicates matters.) HO^- and ClO^- each have a single bonding pair. Their electronic structures are qualitatively the same as those of HF and ClF.

$$\begin{aligned} &HO^-\text{: } (2p\sigma_O+1s_H,\ \sigma)^2(2p\pi_O)^4,\ ^1\Sigma^+ \\ &ClO^-\text{: } (2p\sigma_O+3p\sigma_{Cl},\ \sigma)^2(2p\pi_O)^4(3p\pi_{Cl})^4,\ ^1\Sigma^+. \end{aligned} \tag{6}$$

The wave function of HO^- may also be approximated, by using atomic orbitals, by a mixture of those of $H(V_1)+O^-(V_1)$ and $H^-(V_0)+O(V_0)$. Since the energy at $r=\infty$ is about 4.3 volts lower for the former, and since also the potential energy curve of the former should go down and that of the latter up according to HLPS theory, it appears that the wave function must be nearly pure $H\cdot O^-$. There should, however, be some admixture of $H^+\cdot O^=$, but it is impossible to estimate how much. Comparison with (6) indicates that the bonding orbital $a(2p\sigma_O)+b(1s_H)$ is nearly homopolar ($a=b$), or perhaps shows some inequality $a>b$ if the effect of $H^+\cdot O^=$ is important. Thus it is probable that the strong inequality $a>b$ which is present in this orbital in neutral OH is much reduced by the negative charging of the O atom. (Note that neutral OH differs from OH^- in that one π_O electron is missing from (6).)

In building up the wave function of OCl^- using atomic orbitals, we may consider $O^-(V_1)+Cl(V_1)$, $O(V_0)+Cl^-(V_0)$, and $O^=(V_0)+Cl^+(V_0)$. For $r=\infty$ the first named is probably only a little lower than the second (1.3 volts estimated[6]), but according to HLPS theory its $U(r)$ curve should go down while that of the second should go up. Thus $O^-\cdot Cl$ should predominate strongly over $O\cdot Cl^-$ in the wave function. The importance of $O^=\cdot Cl^+$ is difficult to estimate; it may or may not exceed that of $O\cdot Cl^-$. On the whole, we conclude that the bonding orbital is probably nearly homopolar in ClO^-.

Absorption spectra of OH^- and OCl^- (also SH^- etc.) are known in water solution, but as in the cases of Cl^-, Br^- and I^-, the explanation of these spectra (probably electron removal spectra) is complicated by the presence of the solvent. The most easily removed electron should be the nonbonding $2p\pi_O$ in the case of OH^-, and either $3p\pi_{Cl}$ or $2p\pi_O$ in the case of OCl^-.

Reviewing the results of the preceding discussion, it may be concluded that while the concept of relative electronegativity may possibly always be used, the ordinary scales ($(I+E)/2$ and Pauling's) cannot be used except for normal states of neutral molecules of not too great polarity and with a pair or pairs of bonding electrons. In the case of positive molecule-ions with one bonding electron, I may be used as a measure of electroaffinity.

4. Evaluation of Coefficients in LCAO Molecular Orbitals

Given orbitals ϕ_A and ϕ_B of the two atoms, one can set up a perturbation problem and solve for the energies and the coefficients $a^\times$ and $b^\times$ in the LCAO form Eq. (1). This can be done in the same way for neutral or ionized molecules, provided only the sizes and forms of ϕ_A and ϕ_B are properly chosen. The discussion is also applicable if one or both of the atoms are polyvalent. One or both of the orbitals ϕ_A and ϕ_B may even be *radical* orbitals, i.e., belong to radicals A or B (cf. earlier papers of this series). Or one or both may belong to a *group* of atoms; e.g., ϕ_A may belong to a carbon atom, ϕ_B to the group Cl_4, in the building up of a nonlocalized bonding orbital of CCl_4. The discussion can, however, also equally well be applied to localized orbitals corresponding to the separate C–Cl bonds in CCl_4 (cf. XII of this series).

Corresponding to the two independent orbitals ϕ_A and ϕ_B with which we start, the perturbation problem must of course yield two solutions, say

$$\begin{aligned} \phi_{AB} &= a^\times\phi_A + b^\times\phi_B, \quad \text{with energy } W^\times \\ \phi^*_{AB} &= a^*\phi_A + b^*\phi_B, \quad \text{with energy } W^*. \end{aligned} \tag{7}$$

We assume ϕ_A and ϕ_B each normalized, but note that they are not orthogonal (except for $r=\infty$). They are made both positive in the region where they overlap. Proceeding in the usual way, the secular equation

$$(H_{AA}-W)(H_{BB}-W)-(H_{AB}-SW)^2=0 \tag{8}$$

is found. Here

$$H_{AA}=\int \phi_A H \phi_A dv,\ H_{AB}=\int \phi_A H \phi_B dv,\quad H_{BB}=\int \phi_B H \phi_B dv,\ S=\int \phi_A \phi_B dv. \tag{9}$$

Introducing the abbreviations

$$X=(H_{AA}+H_{BB})/2,\ V=(H_{AA}-H_{BB})/2, \tag{10}$$

the solutions of (8) can be written in the form

$$W(1-S^2)=X-SH_{AB} \pm[(H_{AB}-SX)^2+V^2(1-S^2)]^{\frac{1}{2}}. \tag{11}$$

If atoms A and B are identical, V is zero and (11) reduces to the well-known expression (valid, e.g., for H_2^+)

$$W=(X\pm H_{AB})/(1\pm S). \tag{12}$$

In this case we have

$$a^\times=b^\times=(2+2S)^{-\frac{1}{2}},\ a^*=-b^*=-(2-2S)^{-\frac{1}{2}}; \tag{13}$$

the upper sign in (12) here belongs to $W^\times$, the lower to W^*. Thus ϕ^*_{AB} is the antibonding orbital complementary to the bonding orbital ϕ_{AB}. The quantities $W, X=H_{AA}, H_{AB}$ are all negative and S is positive, at least for the case of ordinary stable molecules and ions in their respective equilibrium states. It should be noted that $X=H_{AA}=H_{BB}$ is considerably lower than the energy of ϕ_A or ϕ_B at $r=\infty$ (all are negative):

$$H_{AA}\equiv(H_{AA})_{r=r}<(H_{AA})_{r=\infty}\equiv W(\phi_A).$$

If atoms A and B are not identical, but the molecule AB (or more accurately, the orbital ϕ_{AB}) is known to be slightly or moderately polar, (12) and (13) should still be roughly true. We may then expand (11) in terms of the quantity V which vanishes when $A\equiv B$. Similarly, the quantities $a^\times-b^\times$ and a^*+b^*, or $(a^\times/b^\times)-1$ and $(-a^*/b^*)-1$, may be expanded in powers of V. For the energy, one gets

$$W=(X\pm H_{AB})/(1\pm S) \pm V^2/2Y\mp V^4(1-S^2)/8Y^3+\cdots, \tag{14}$$

where

$$Y=H_{AB}-SX. \tag{15}$$

From the perturbation theory equations, one finds

$$a/b=(W-H_{BB})/(H_{AB}-SW) =(W-X+V)/(H_{AB}-SW). \tag{16}$$

Substituting for W according to Eq. (14), expanding again, and making use of the normalization condition

$$a^2\pm 2Sab+b^2=1, \tag{17}$$

and with the upper signs in Eqs. (14), (17), (18)

for $a^\times$, $b^\times$, the lower for a^*, b^*, one finally arrives at

$$\begin{aligned} a(2\pm 2S)^{\frac{1}{2}} &= \pm 1+(1\pm S)R/2\pm(S^2-1)R^2/8 \\ &\quad -3(1\pm S)(1-S^2)R^3/16+\cdots, \\ b(2\pm 2S)^{\frac{1}{2}} &= 1\mp(1\pm S)R/2+(S^2-1)R^2/8 \\ &\quad \pm 3(1\pm S)(1-S^2)R^3/16+\cdots, \end{aligned} \tag{18}$$

where $$R=V/Y=V/(H_{AB}-SX). \tag{19}$$

In particular, the coefficients $a^\times$, $b^\times$ of ϕ_{AB} are

$$\begin{aligned} a^\times(2+2S)^{\frac{1}{2}} &= 1+(1+S)R+\cdots, \\ b^\times(2+2S)^{\frac{1}{2}} &= 1-(1+S)R+\cdots, \end{aligned} \tag{20}$$

and

$$a^\times-b^\times = [(1-S)/2]^{\frac{1}{2}}R\{1-3(1-S^2)R^2/8+\cdots\} \tag{21}$$

$$a^{\times 2}-b^{\times 2}=R\{1-(1-S^2)R^2/2+\cdots\}. \tag{22}$$

Since we have taken $a^\times=b^\times$ or $a^{\times 2}=b^{\times 2}$ as a criterion of equality of electroaffinity of atoms A and B (or more strictly, of ϕ_A and ϕ_B), we see from Eqs. (21), (22) that the quantity R, of which the vital factor is V, is some sort of measure of the difference in electroaffinity of atoms A and B. Let N represent "absolute electroaffinity." It will be shown below that, although no unique definition can be given, any quantity such as $-V$, $-V(-Y)^{\frac{1}{2}}$, or $-V/-Y\equiv R$, usually may reasonably be identified with (N_A-N_B), because of the usual rough constancy in practice of Y. At any rate, the *sign* of (N_A-N_B) is determined by that of $-V$.

At this point it may be noted that Y in Eq. (19) is negative in practice; H_{AA} and H_{BB} are also negative; hence $V(\equiv(H_{AA}-H_{BB})/2)$ is negative when R is positive, and *vice versa*. Now N is by definition positive, and larger for a more electronegative atom. Hence finally, positive (N_A-N_B) must correspond to positive R and negative V.

Before going further with the discussion of the "normal" case in which Y is fairly constant, it may be noted that if for any reason $-Y$ should be unusually small, R and so the difference between a and b (cf. Eq. (21)) will tend to be increased. That is, for a given difference in electronegativity, or at any rate for a given V, the polarity of a molecule tends to be greater if the strength of the bond (measured approximately by $-Y$) is weaker. Also, when Eqs. (18)–(22) are applied to the polyatomic case, and when we use nonlocalized molecular orbitals for the latter, the quantity Y is found to depend not only on bond strength but also on bond angles. This introduces an additional factor tending to affect the values of a and b (cf. discussion of H_2O in XII of this series).

It may be well at this point to dispose of the question as to whether our results will lack significance because of the roughness of the LCAO approximation for molecular orbitals. It is important to note that even though the LCAO form may be greatly distorted as compared with the real orbital, the degree of polarity should apparently be correctly represented (especially if we are guided by empirical electroaffinity scales rather than theoretically calculated R's) in either of two limiting cases, namely $a^2=b^2$ (homopolar) and $a=1$, $b=0$ or $a=0$, $b=1$ (extreme heteropolar). In intermediate cases, the sign of the polarity should always be correct, and even its magnitude should be less in error than are other characteristics of the LCAO form.

5. Theoretical Basis of Pauling's Electronegativity Scale

Before going farther with a consideration of the a's and b's, it will first be shown that Eq. (14) affords a theoretical explanation of the basis of Pauling's electronegativity scale. Let P_A-P_B be the relative electronegativity of atoms A and B on this scale. The latter is based on the empirical relation[5]

$$(P_A-P_B)^2+\cdots=\Delta_{AB}, \tag{23}$$

where $$\Delta_{AB}=D_{AB}-\tfrac{1}{2}(D_{A_2}+D_{B_2}). \tag{24}$$

Here D is the energy of dissociation, in electron volts, of a molecule or bond. Insofar as the theorem[5] of the "additivity of normal covalent [i.e., homopolar] bond energies" holds good, Δ_{AB} should, as Pauling showed, always be positive and should be a measure of the departure of the A–B bond from the pure homopolar type. In practice, the Δ's proved to be indeed positive in the cases cited,[5] and proved amenable to interpretation in terms of a linear scale of electronegativities P in accordance with the empirical Eq. (23).

A theoretical explanation of the form of Eq.

(23) has not been given hitherto, but may be obtained as follows. The total energy of a molecule AB in its normal state can be expressed by $W^t = W^i + 2W$ with W given by Eq. (14), using the upper signs in this equation. $2W$ then refers to the pair of bonding electrons, and W^i to the remaining energy. It is now readily seen that

$$\Delta_{AB} = -W^t{}_{AB} + \tfrac{1}{2}(W^t{}_{A_2} + W^t{}_{B_2}). \quad (25)$$

We note that in Eq. (14) as applied to a molecule A_2 or B_2, $V=0$. Putting $[(X+H_{AB})/(1+S)]=K$ in Eq. (14), and $W^i+2K=L$, Eq. (25) now yields

$$\Delta_{AB} = \{-L_{AB} + \tfrac{1}{2}(L_{A_2} + L_{B_2})\} + V^2/-Y - V^4(1-S^2)/(-4Y^3) + \cdots. \quad (26)$$

Now if Pauling's theorem of the additivity of homopolar bond energies is valid, the expression in braces must be equal to zero, and we get

$$\Delta_{AB} = aV^2 - bV^4 + \cdots, \quad (27)$$

with $a=-1/Y$, $b=(1-S^2)/(-4Y^3)$, the coefficients a and b being positive. The argument leading to Eq. (27) can be extended to show that the latter should hold also for polyatomic molecules.

Eq. (27) is in complete agreement with Pauling's empirical Eq. (23), and the foregoing discussion gives a theoretical derivation of the form of Eq. (23), and also shows that

$$(P_A - P_B) = (-Y)^{-\frac{1}{2}}(-V) = -\tfrac{1}{2}(-Y)^{-\frac{1}{2}} \times (H_{AA} - H_{BB}). \quad (28)$$

This permits the following definition of the "absolute electroaffinity" P on Pauling's scale, a quantity not considered by Pauling:

$$P_A = \tfrac{1}{2}(-Y)^{-\frac{1}{2}}(-H_{AA}). \quad (29)$$

All these results depend of course on the validity of the theorem of the additivity of homopolar bond energies. This theorem is an empirical one, and is undoubtedly not exact.[5] The best evidence for its correctness is really the approximate empirical validity of Eq. (23) in most cases.*

The exact validity of Eqs. (27)–(29) with a definite constant P value for each atom would imply that the quantity $-Y$, which depends on both the atoms A and B, must be a universal constant. Since this is certainly not exactly true, it is clear that the P values are inherently incapable of representing exactly definable properties of atoms, but must be rough averages based on an average value of $(-Y)^{-\frac{1}{2}}$. The lack of definiteness of P scale values is also affected by the fact that H_{AA} in Eq. (29) is far from being independent of the second atom B.

The success of Eq. (23) suggests that Y is in practice fairly constant in ordinary cases. This is understandable so long as we deal with molecules not differing too greatly in bond strength, since $-Y$ should generally be roughly proportional to the latter. The effects of Y variation are also diminished because P depends on $(-Y)^{\frac{1}{2}}$.

For large values of $(P_A - P_B)$, Eq. (27) predicts that Δ_{AB} should be *less* than aV^2. This is in accordance with findings of Pauling on strongly polar molecules: for H_2O there is an appreciable deviation from Eq. (23) in the sense of Eq. (27), and in HF there is a large deviation. For really heteropolar molecules (diatomic NaCl, etc.) it is clear that the approximations involved in Eqs. (14), (27), (29), etc. break down completely. Thus the whole basis of Pauling's (also of the writer's) N scale breaks down in such cases. Nevertheless, it so happens that polarities and Δ's usually tend still to increase monotonically with $(N_A - N_B)$ even when Eqs. (27), (29) no longer hold, so that the N scales can still usually be used empirically in a qualitative way. This is true, for example, for ordinary diatomic salt molecules like NaCl, but apparently not, as regards Δ, for certain less polar salt molecules like LiH where apparently the additivity theorem for homopolar bond energies fails completely.*

Some readers may be dissatisfied with the foregoing analysis, in particular with the theoretical justification of the form of Eq. (23), on the ground that the use of LCAO molecular orbitals gives too poor an approximation. The writer has therefore carried through the analysis again using atomic orbitals (HLPS wave functions combined with ionic functions),[5, 6] and finds in place of Eq. (27) a similar equation in which Δ_{AB} again comes out approximately proportional to the square of

* A case where Eq. (23) apparently fails completely is that of diatomic LiH, where Δ_{AB} is apparently negative, although it should have a large positive value as judged by $N_H - N_{Li}$ on the writer's electroaffinity scale, where $N_H - N_{Li}$ is comparable with $N_F - N_H$. To be sure, the value of D for LiH is not very sure, yet the error in it can hardly be large enough to make LiH conform to Eq. (23).

a quantity which must be identified with (P_A-P_B) of Eq. (23). The details of the analysis will not be given here, since they are considerably more complicated than those of the analysis above, but lead to essentially the same result.

6. Electroaffinity Scales and LCAO Coefficients

By referring to Eqs. (27), (19), (21), (22) it will now be seen that all of the quantities $\Delta^{\frac{1}{2}}$, $(a^{\times}-b^{\times})$, and $(a^{\times 2}-b^{\times 2})$ can be expressed in the form

$$k(P_A-P_B)-l(P_A-P_B)^3,$$

where k and l are different for each of the three quantities, but should be fairly constant for any one insofar as Y and S are constant. (S should be fairly constant if Y is.) Our discussion does not show for which of the three quantities the k and l will be the more nearly constant. The equations for the three cases are as follows:

$$\Delta^{\frac{1}{2}}=(P_A-P_B)-[(1-S^2)/(-8Y)]\times(P_A-P_B)^3+\cdots, \quad (30)$$

$$(a^{\times}-b^{\times})=(b^*+a^*)=[(1+S)/(-2Y)]^{\frac{1}{2}}\times(P_A-P_B)-(3/-8Y)(1-S^2)[(1+S)/(-2Y)]^{\frac{1}{2}}\times(P_A-P_B)^3+\cdots, \quad (31)$$

$$(a^{\times 2}-b^{\times 2})=(b^{*2}-a^{*2})=(-Y)^{-\frac{1}{2}}(P_A-P_B)-\tfrac{1}{2}(1-S^2)(-Y)^{-1\frac{1}{2}}(P_A-P_B)^3+\cdots. \quad (32)$$

It may be well to point out that, because of the roughness of the LCAO approximation used in deriving Eqs. (30)–(32) and other equations, one can hardly hope to attach quantitative significance to their coefficients. The forms of these do, however, possess at least suggestive value.

It will be seen that, instead of defining $N=P$ as in Eq. (29), which makes $k=1$ for $\Delta^{\frac{1}{2}}$, we might have defined N so as to make $k=1$ for $(a^{\times}-b^{\times})$, or for $(a^{\times 2}-b^{\times 2})$. Such definitions of N would be those naturally suggested by Eqs. (21), (22). It will be simpler, however, to keep to the Eqs. (28)–(29) definition, since then we can use Pauling's scale values directly, also because P involves Y only as $(-Y)^{-\frac{1}{2}}$, while for the other definitions, N would involve $(-Y)^{-1}$.

One wonders, however, whether it might not be possible to find an N scale on which the scale value for an atom A could be made more nearly independent of atom B than is the case for the P or other scales suggested above. Quite possibly such an improved scale could be found, but until the nature of the dependence of H_{AA} and Y on atom B has been more carefully investigated, we can hardly expect to set it up with confidence. Besides, our above analysis of possible N scales makes it fairly clear that it is inherently impossible to consider the electroaffinity N of an atom as an exact atomic property; even at best, N must be admitted to vary somewhat with the nature of other atoms in the molecule.

Nevertheless, the writer has in a previous paper[6] set up a scale of "absolute electroaffinity" in which N, which may here be called M to distinguish it from P or other possible N definitions, is given by

$$M=(I+E)/2 \quad (33)$$

for any atom. Although Eq. (33) gives a means of assigning a definite number M for the electroaffinity of each atom, its theoretical justification as a measure of electroaffinity can apparently be given only very roughly (reference 6; section 2 above; and below). Its best justification so far is perhaps its empirical agreement in certain simple cases with Pauling's empirical approximate scale of P's relative to P_H, the numerical relation between the two scales[6] being, empirically,

$$(M_A-M_B)=2.78(P_A-P_B), \quad (34)$$

with P in (volt electrons)$^{\frac{1}{2}}$, M in volt electrons.

It is possible, in the case of neutral diatomic molecules with one electron-pair bond, to establish a rather illuminating connection between the quantity (M_A-M_B) and the quantity $-V$ of Eqs. (19), (21), and so with (P_A-P_B) of Eq. (28). Recalling that $-V=-(H_{AA}-H_{BB})/2$, we note that H_{AA} and H_{BB} are energies of ϕ_A and ϕ_B as calculated when atoms A and B are close together and in each other's fields ($r=r_e$). If taken for $r=\infty$, $-(H_{AA}-H_{BB})/2$ (let us call this $-V_\infty$) would be equal to half of T_A-T_B, the difference between the term values of ϕ_A and ϕ_B each calculated for a separate central field.

Referring to the last paragraph of section 2, it will be seen that T_A and T_B here refer not to force centers with equal net charges $+\frac{1}{2}e$ (let T_A, T_B for the latter case be called $T^0{}_A$, $T^0{}_B$), but to centers in which a net charge, say Q, has been

displaced from A to B. If, roughly, we put

$$T=RZ^{*2}/n^2, \text{ then } dT/dZ^*=2T/Z^*.$$

Now the effect of charge Q, approximately, is to alter Z^* by an amount $dZ^*_B=aQ/e=-dZ^*_A$, where $a=0.35$ approximately (Slater), noting that Q goes into the outer shell. From this we find, approximately,

$$T_A=T^0_A(1-2a_AQ/eZ^*_A); \qquad T_B=T^0_B(1+2a_BQ/eZ^*_B).$$

As will be shown in the next section, $Q/e=(a^{\times 2}-b^{\times 2})$ for an electron-pair (cf. Eq. (39)), or *half* this in our case where are interested in the Hartree field corresponding to one electron of the pair. Hence, using Eqs. (22), (19), (10),

$$Q/e=(T_A-T_B)/-4Y+\cdots.$$

Combining this with the equations just given for T_A and T_B, one finds

$$T_A-T_B=C(T^0_A-T^0_B), \tag{35}$$

where

$$C=\{1+[(a_AT^0_A/Z^*_A)+(a_BT^0_B/Z^*_B)]/-2Y\}^{-1}. \tag{36}$$

In practice, C is less than, but probably in rough approximation equal to, unity.

From Eq. (35), it will be seen that T_A-T_B, hence $-V_\infty$, is proportional to $T^0_A-T^0_B$, insofar as C is constant. Further, it is plausible that $-V$ of Eq. (19) ($r=r_e$) is approximately proportional to $-V_\infty$ under ordinary circumstances. (Note that for A≡B, $H_{AA}-H_{BB}$ vanishes simultaneously at all values of r.) Now as we have seen in section 2, T^0_A and T^0_B are approximately equal or proportional to the quantities $(I+E)/2$ of neutral atoms A and B. Hence $-V$ may plausibly be expected to be approximately proportional to M_A-M_B. Now, however, according to Eq. (28), $-V$ is also approximately proportional to (P_A-P_B). Thus it is shown by theoretical considerations, although not rigorously, to be at least plausible that (M_A-M_B) should be proportional to (P_A-P_B), in agreement with the empirical Eq. (34).

The above justification of the M scale refers to neutral molecules composed of uniunivalent atoms A, B. Complications arise when one extends the argument to polyatomic molecules (cf. also the discussion in reference 6). Although it is likely that the use of the M scale could be justified also in such cases, we shall for the present use the P scale for these. The theoretical basis given for the P scale in section 5 appears to be equally valid if A and/or B is polyvalent. Empirically also, the P scale has been established for several polyvalent atoms, in the case of single bonds.

In concluding this section, some qualitative applications of Eq. (31) will be mentioned. Consider for example the σ bonding orbital (cf. Eqs. (7)) of a molecule XY (X, Y=halogen atoms)[8]:

$$\sigma=a^{\times}(3p\sigma)_{Cl}+b^{\times}(5p\sigma)_I+\cdots; \qquad \sigma^*=a'(5p\sigma)_I-b'(3p\sigma)_{Cl}+\cdots. \tag{37}$$

Here the a's and b's can all be chosen positive. If YX=ClI, ClBr, BrI, etc., then from the P scale, $a^{\times}>b^{\times}$ and $a'>b'$ in each case, and the quantities a/b are greater for ClI than for ClBr. Similarly, if AB=XH, we see that $a/b>1$ throughout, increasing in the order IH, BrH, ClH, FH.

7. Charge Distributions and Relative Electronegativities

Given two electrons occupying a bonding orbital ϕ_{AB} (Eqs. (1) or (7)), the corresponding mean charge density is given by $-2e(\phi_{AB})^2$, a function in space. By drawing a boundary surface somewhere between the two atoms (obviously a mid-plane if A≡B) one might seek to find how much of the total charge $-e$ belongs to each atom, and from this to determine a net charge for each. Incidentally, one might define the difference in electronegativity of two atoms as proportional to the above-determined net mean charge transferred from the one to the other. This definition is essentially equivalent, for *small* or moderate (N_A-N_B) values, to those discussed in section 6.

Unfortunately no rule free from arbitrariness can be set up for drawing a boundary surface between A and B, except in the case A≡B. The difficulty appears in enhanced form in more complex molecules, e.g., when one tries to allocate net charges to the various atoms in ClO_4^-. This difficulty is an example of the essential impossibility of giving exact definitions without arbitrariness for any atomic property, e.g.,

electroaffinity or atomic or ionic radius, for an *atom in combination.*

In the diatomic case, a fairly natural even though arbitrary procedure for dividing the bonding electrons' charge can be set up. Consider the following equation, obtained by using Eqs. (7), (9) and (17):

$$-2e=-2e\int(\phi_{AB})^2dv=-2e(a^{\times 2}+2a^{\times}b^{\times}S+b^{\times 2}). \quad (38)$$

A reasonable procedure would be to assign the amount of bonding electron charge $q_A=-2e(a^{\times 2}+a^{\times}b^{\times}S)$ to atom A, $q_B=-2e(a^{\times}b^{\times}S+b^{\times 2})$ to atom B. Since the net charge on each atom is $+e$ if the two bonding electrons are omitted, the actual net charges Q are obtained by taking $Q=q+e$. With the help of Eq. (17), one then gets

$$Q_A=-e(a^{\times 2}-b^{\times 2})=-Q_B. \quad (39)$$

One notes that Eq. (39) gives $Q_A=0$ for $a^{\times}=b^{\times}$, $Q_A=\mp e$ for $a^{\times}=1$, $b^{\times}=0$ or $a^{\times}=0$, $b^{\times}=1$, as it should. Incidentally, it may be mentioned that the ideal heteropolar case $a^{\times}/b^{\times}=0$ or $b^{\times}/a^{\times}=0$ cannot be realized unless ϕ_A and ϕ_B are orthogonal, i.e., $S=0$, which in practice is not likely to be more than approximately true for a stable molecule. (Cf. Eq. (16) for a/b or b/a, noting that H_{AB} in general vanishes if and only if S does.)

Combining Eq. (32) with Eq. (39) one gets

$$-Q_A/e=k'(P_A-P_B)-l'(P_A-P_B)^3+\cdots, \quad (40)$$

where k' and l' are both positive, with $k'=(-Y)^{-1}$, $l'=\frac{1}{2}(1-S^2)(-Y)^{-1\frac{1}{2}}$, and $l'/k'=(1-S^2)/(-2Y)$. Eq. (40), which is based on the expansions Eqs. (18), is valid only if $|Q/e|$ is not too large (say $|Q/e|<\frac{1}{2}$). For heteropolar molecules (say $\frac{1}{2}<|Q/e|<1$), Eq. (40) could be replaced by another expression based on expansion of Eq. (16) about the case $a=1$ or $b=1$. This range of cases will, however, not be considered here.

As can be seen from the discussion in section 6, we may expect k' and l' to be roughly constant in ordinary cases. If we could estimate their values, Eq. (40) should give interesting information as to the Q's of various bonds, and might also be helpful in interpreting dipole moment data.

In estimating k' and l', we might try to make use of Pauling's conclusion[10] that HF is about half-way between the homopolar and the ideal heteropolar case. Half-way would mean $a^{\times 2}$ half-way between $1/(2+2S)$ and 1, $b^{\times 2}$ half-way between $1/(2+2S)$ and 0 (cf. Eqs. (20)). This gives $a^{\times 2}-b^{\times 2}=\frac{1}{2}$, hence $Q_F=-\frac{1}{2}e=-Q_H$ according to Eq. (39). At the same time, (P_F-P_H) is about 2.00 according to Pauling.[5]

Unfortunately, the polarity of HF is so strong that the term in $(P_A-P_B)^3$ in Eq. (40) can hardly be ignored. If, however, we do neglect it for the moment, we find $k'=0.25$. Actually this gives only a *lower limit* for k', since the term in $(P_A-P_B)^3$ is negative. For a guess (to be tested later), suppose $l'=1/48$; then to get $Q_F=-0.50e$ for HF with $P_F-P_H=2.00$, $k'=1/3$ is required. That is,

$$Q_B/e=-Q_A/e=(P_A-P_B)/3-(P_A-P_B)^3/48. \quad (41)$$

Instead of making a guess, however, we might try to estimate the ratio l'/k', with the help of Eq. (30), from the experimental Δ value[5] ($\Delta^{\frac{1}{2}}=1.66$) for HF. Substituting this, also $(P_F-P_H)=2.00$, in Eq. (30), one gets $(1-S^2)/(-8Y)=0.34/8$ for HF. But now l'/k' in Eq. (40),—see above,—should be $(1-S^2)/(-2Y)$. Hence $l'/k'=0.17$. We now have sufficient information to determine both k' and l', and get

$$Q_B/e=0.76(P_A-P_B)-0.13(P_A-P_B)^3. \quad (41a)$$

Unfortunately this equation cannot be correct, since it gives absurd results (Q larger for the NH and OH bonds than for HF). This may be attributed partly to uncertainty in the P scale value for F, but is perhaps mainly a result of the roughness of the LCAO approximation; in particular, it is probable that the ratios l'/k' calculated using Eqs. (30), (32), (40) are badly in error because of the inadequacy of the approximation. It is of interest to note that if Eq. (41a) were correct, the quantities Y and S could be calculated from its coefficients (see text near Eq. (40)). Eq. (41a) thus gives $-Y=1.72$ volts, which is probably far too small; it also gives $S^2=0.42$, a not unreasonable value.

Since l'/k' should be constant, it should be possible to calculate it again, in the same manner as above, using Pauling's data on the O—H bond, where $\Delta^{\frac{1}{2}}=1.326$, $(P_O-P_H)=1.40$. Combining the l'/k' ratio so obtained ($l'/k'=0.11$, which it

[10] L. Pauling, J. Am. Chem. Soc. **54**, 988 (1932).

will be noted is *not* the same as before) with the HF data $Q_H/e=\frac{1}{2}$ and $P_F-P_H=2.00$, one gets

$$Q_B/e=0.44(P_A-P_B)-0.0475(P_A-P_B)^3. \quad (41b)$$

This gives much more reasonable Q's for the NH and OH bonds, but still too large. Also, it gives $-Y=5.2$ volts, better than before, but it gives $S^2=-0.11$, which is impossible.

It appears necessary to abandon any attempt to estimate l'/k' theoretically by the use of Eqs. (30) or otherwise. We may, however, with some confidence rely on the theoretical derivation of the *form* of Eq. (40), and on the rough constancy of k' and l', which is related theoretically to the existence of the P scale.

If the result $Q/e=\frac{1}{2}$ for HF can be approximately trusted, and if k' and l' are approximately constant, we now know that the correct Eq. (40) must lie somewhere between Eq. (43), where l' is surely too large, and the equation

$$Q/e=0.25(P_A-P_B),$$

obtained by setting $l'=0$. We are thus led by a trial and error process back to an equation with coefficients about as given in the "guess" Eq. (41). We may now seek to test the correctness of the coefficients in Eq. (41) by seeing, if possible, whether it gives correct Q's for other cases than HF. Our main difficulty is that at present we have no source of accurate Q's, either empirical or theoretical.

8. Dipole Moments and Relative Electronegativities

If used with caution, electric moment data for simple molecules (HCl, H_2O, NH_3 etc.) should help us by giving *lower limits* for Q's. For a diatomic molecule in which only the bonding-electron pair contributes to the electric moment, the latter should be readily calculable in LCAO approximation. The mean distribution of electricity as given by Eq. (38) for the two bonding electrons comprises (a) a charge $-2ea^{\times 2}$ centered around atom A; (b) a charge $-4ea^{\times}b^{\times}S$ centered around a point between A and B; (c) a charge $-2eb^{\times 2}$ centered around B. If the distance between the centers A and B is r_e, and the distance of the electric center of item (b) from the midpoint (to be taken as origin) of the line A$\longleftrightarrow$B is z, then the net electric moment of AB corresponding to items (a), (b), (c) plus a charge $+e$ on each atom, is

$$\mu=er_e(a^{\times 2}-b^{\times 2})-4eza^{\times}b^{\times}S. \quad (42)$$

Positive μ is taken as corresponding to polarity A^-B^+, which exists if $a^{\times 2}>b^{\times 2}$. The positive z direction is taken as the direction A$\rightarrow$B.

To the *primary* (bonding-pair) dipole moment given by Eq. (42) must be added the secondary moment induced in the nonbonding electrons, say μ_S. Including this and also substituting from Eq. (39), we get

$$\mu_{AB}=Q_Br_e-(4eza^{\times}b^{\times}S-\mu_S). \quad (43)$$

Of considerable interest is the "homopolar dipole" term $4eza^{\times}b^{\times}S$, whose presence discloses the hitherto perhaps unsuspected fact that molecules which fulfill the criterion of homopolar bonding ($a^{\times}=b^{\times}$) may still have a dipole moment. This of course does not apply to strictly homopolar molecules (A$\equiv$B), where $z=0$, but in all other cases the homopolar dipole term must be present and may be fairly large. Its magnitude increases with inequality in *size* of the two atoms, which is measured by z. Its sign is such that its positive pole is always directed toward the larger atom. Thus it may either assist or oppose the main dipole term Q_Br_e. For instance in the hydrogen halides, with the barely possible exception of HF, it opposes the main dipole term. In turn, however, it may often be opposed by μ_S; examination of the μ data on the hydrogen halides indicates that μ_S there opposes and partially cancels $4eza^{\times}b^{\times}S$ (see below).

It may perhaps be well to state at this point that an equation similar to Eq. (39), but more complicated, can be developed using atomic orbitals[5, 6] (HLPS method) for describing the electronic structure of AB; the equation includes a term in $(\alpha^2-\beta^2)$, corresponding to $(a^{\times 2}-b^{\times 2})$ in Eq. (39). Likewise equations identical in form with Eqs. (40) and (41) can be obtained. Further, equations for μ corresponding to Eqs. (42), 43) can be obtained, but are considerably more complicated. It is especially to be noted that a homopolar dipole term again appears in these, and is of the same order of magnitude as in Eqs. (42), (43). Thus even though our approximation based on LCAO molecular orbitals may be

poorer than one using atomic orbitals, there is no reason to doubt that the conclusions reached here as to Q's and μ's are qualitatively sound.

Returning to Eq. (43), we shall wish to apply this to simple polyatomic molecules like H_2O and NH_3. It is probably safe, as an approximation, to use Eq. (43) for each bond separately in such a molecule. Also it is probably safe to say, in the cases of H_2O and NH_3, that if we take μ_{AB}/r_e for a bond (OH or NH), this will give a *lower limit* for Q_B. For there is little doubt that H is effectively smaller in size than O or N (e.g., Pauling[11] gives 0.29A for the radius of H, 0.66A and 0.70A for O and N respectively), so that the homopolar dipole will oppose the main dipole; while μ_S, even if opposed to the homopolar dipole and so assisting $Q_B r_e$, is doubtless smaller than the homopolar dipole.

In Table I a comparison is made between the

TABLE I. *Effective charge on H atom.*

Molecule	$\mu\times10^{18}$	Bond angle	$\mu_{AH}=\mu$ per bond ($\times10^{18}$)	Q_H/e μ_{AH}/er_e	Q_H/e Eq. (30)
HF	—		—	—	0.50
H_2O	1.85	105°	1.53	0.33	0.41
NH_3	1.49	107°	1.33	0.27	0.30
HCl	1.03		1.03	0.17	0.30

Notes. Cf. reference 6, Table I. In the case of NH_3, the H−N−H bond angle is revised, the new value being based on calculations from band spectrum data, giving, respectively, 0.38A and 1.02A as the height and length of the NH_3 pyramid (cf. M. F. Manning, J. Chem. Phys. **3**, 136 (1935) and references there given).

values of Q_H/e calculated from Eq. (41) for the A−H bonds in NH_3, H_2O and HCl, and the lower-limit values of Q_H/e obtained in accordance with the foregoing discussion by taking μ_{AH}/er_e. Although we can do little more than guess how much the true values of Q_H should exceed the lower-limit values, it would seem from Table I that the values obtained from Eq. (41) are fairly reasonable. At any rate, it appears probable that we shall commit no gross error in using Eq. (41) to roughly estimate Q's, also $a^\times$'s and $b^\times$'s (cf. Eq. (39)) in following papers of this series. If anything, it seems likely that k' in Eq. (43) should be increased, so as to give somewhat larger Q_H's; thus Q/e for HF may well be as large as 0.55 or even 0.60 instead of the 0.50 assumed above.

Digressing for a moment from the main object of the present paper, it may be remarked that the extension of Table I to HBr, HI, and various other molecules seems to offer some possibility of throwing new light on dipole moments, although further study and refinement of the method are first needed. It might be better to use the Q expressions obtained from approximations using HLPS electronic structures (atomic orbitals only).

It is easy to estimate the homopolar dipole term in Eq. (43) or in the corresponding equation based on atomic orbitals, by using Pauling's empirical atomic radii[11] to estimate z, and estimating S from Heitler-London calculations. This homopolar term is often found to be larger than the main term Qr_e (using Eq. (41)), e.g., in HI (by both molecular and atomic orbital methods). Since its sign in, e.g., HI is opposite to that of Qr_e, one must assume that μ_S of Eq. (43) comes to the rescue and largely cancels the homopolar term, leaving, however, for μ a net observable result which is still much less than Qr_e.

In the molecules HX, this net deficit of μ compared with Qr_e apparently increases steadily from HF to HI. This makes it qualitatively possible that the actual μ can be approximately proportional to Q, hence by Eq. (41) to (P_A-P_B). Such a situation would afford an explanation of the parallelism of μ_{AH} to (P_A-P_H) noted by Malone and used by him as a basis for the electric-moment scale[12] of relative electronegativities. The present analysis indicates that this parallelism is somewhat fortuitous, and that it probably would not hold in general; hence that the electric-moment scale of electronegativities is less significant than the other scales. As a matter of fact, the agreement between Pauling's scale and the electric moment scale is much less good for O and especially N than Malone supposed, when the band spectrum values of the HOH and HNH angles are used (cf. Table I of reference 6, note f, in regard to μ_{OH}, and cf. the revised value for μ_{NH} in the present Table I).

[11] L. Pauling, Proc. Nat. Acad. Sci. **18**, 293 (1932).

[12] J. G. Malone, J. Chem. Phys. **1**, 197 (1933).

Electronic Structures of Molecules

XII. Electroaffinity and Molecular Orbitals, Polyatomic Applications

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The use of electroaffinity data in the approximate estimation of the polarity coefficients of molecular orbitals and of the effective charges on atoms in polyatomic molecules is illustrated by application and extension of the results of XI of this series. Applications are made especially to CH_4, CX_4 and H_2O, also to CH_3X, NH_4^+, ClO_4^-, etc. Electronic structures are given first using localized, later using nonlocalized molecular orbitals. Comparisons are also made with Slater-Pauling electron configurations. Among tetrahedral molecules RA_4, the homopolar part of the valence is shown to be in some cases nearly all s, in others nearly all p valence; in others both; and a varying part of the valence is heteropolar. Consideration of these facts suggests that the special stability of the tetrahedral type RA_4 should be attributed rather to close packing associated with coordination number four than to special properties of the mixture of s and p valence.

1. LOCALIZED MOLECULAR ORBITALS

The treatment given in XI of this series[1] was there applied primarily to diatomic molecules AB. It can be extended to polyatomic molecules in either of two ways, namely, (*a*) by assigning the two electrons of each chemical bond to a diatomic type molecular orbital localized in the region of the bond (Hund method[2]), or (*b*) using nonlocalized molecular orbitals (present method). The former method is considered in this section, the latter in the next.

Insofar as we can consider the several bonds going out from a single atom as independent, the methods and equations of XI can be directly applied in determining a's and b's and Q's for the localized orbitals of the Hund method. Since Pauling's relative electronegativity values $(P_A - P_B)$ for polyvalent atoms refer to these atoms while exerting their full valence, these values should be suitable for use in Eq. (41) of XI, i.e., the mutual influences of the several valence bonds going out from any atom have already been discounted. Naturally this discounting can represent only a rough average. More exactly, the electronegativities of atoms, and the Q's developed at the ends of bonds, cannot be entirely independent of the nature of the other atoms and bonds present in the same molecule.

Further, if one should deal with the same atoms in varying valence stages, one would in general expect a different electroaffinity for each stage. There are indications, however, that these differences are not great so long as only the *number*, but not the *type* (s, p, etc.) of the valence is altered. If the type is altered, the electroaffinity may change considerably.[3]

The discussion of polarity coefficients and Q's for localized orbitals in this section is of interest not only in itself but also as a preparation for the somewhat more complicated case of nonlocalized orbitals in the next section. At the same time, it affords an opportunity of making comparisons, in respect to the description of polarity, between molecular wave functions constructed using molecular orbitals, and molecular wave functions based on atomic orbitals alone. In making these comparisons, a few simple molecular types RA_n, in particular H_2O, CH_4, and CX_4, will be used as examples.

Using atomic orbitals (Slater-Pauling method) the normal state of H_2O (symmetry C_{2v}) appears as

$$1s_O^2 2s_O^2 (2p_{y'})_O \cdot (1s_H)(2p_{z'})_O \cdot (1s_H)(2p_x)_O^2, {}^1A_1. \quad (1)$$

The bonds are formed between $(2p_{y'})_O$ and $1s$ of one H, and $(2p_{z'})_O$ and $1s$ of the other H. The pair $(2p_x)_O^2$ are nonbonding electrons. The axes y' and z' are taken so that the bisector of the 90° angle between them coincides with the bisector of the actual 105° angle of H−O−H. The fact that the total electron state can belong to a representation (here A_1) of the symmetry group of the molecule, even though the atomic orbitals do not belong to such a representation,

[1] R. S. Mulliken, J. Chem. Phys. this issue: XI of this series.

[2] F. Hund, Zeits. f. Physik **73**, 565; **74**, 1, 429 (1932).

[3] R. S. Mulliken, J. Chem. Phys. **2**, 782 (1934).

has been discussed in IV of this series,[4] section 2. Similar remarks apply to configuration (2) and others similarly expressed below.

Using Hund molecular orbitals for the bonding electrons, we have

$$1s_O^2 2s_O^2[(2p_{y'})_O+(1s_H)]^2[(2p_{z'})_O+(1s_H)]^2(2p_x)_O^2,\ ^1A_1. \quad (2)$$

Here $[(2p_{y'})_O+(1s)_H]$ may be considered as an abbreviation for $a(2p_{y'})_O+b(1s)_H$, an LCAO approximation to an H−O bonding molecular orbital; or better as a brief suggestive symbol for a "real" molecular orbital[5] whose exact details are not yet known. From the relative electronegativities of H and O, it is clear that a very considerably exceeds b. The same values of a and b hold for the z' orbital, which is geometrically and physically equivalent to the y'.

The degree of polarity of the bonds can be roughly expressed in terms of the amount of negative charge displaced from H to O. According to Eq. (41) of XI, with $P_O-P_H=1.40$,[6] we get $Q_H=+0.41e$. Considering both bonds, the total polarity may be expressed roughly by writing $(H^{+0.4})_2O^{-0.8}$.

The electron configuration (2) has a great advantage over (1), at least conceptually, in that it can be made to correspond to the actual strong polarity in the O−H bonds, whereas (1) corresponds to pure homopolar bonds. This disadvantage of (1) can be overcome only by writing additional electron configurations involving ionic binding, of which the most important are

$$(1s)_O^2(2s)_O^2(2p_{y'})_O^2(2p_{z'})_O\cdot(1s_H)(2p_x)_O^2,\ ^1A_1,$$
$$(1s)_O^2(2s)_O^2(2p_{y'})_O\cdot(1s_H)(2p_{z'})_O^2(2p_x)_O^2,\ ^1A_1, \quad (3)$$

belonging to HO^-H^+. Then the actual wave function for the normal state of H_2O must be taken as a linear combination of wave functions corresponding to (1) and (3) (and others), with coefficients to be determined, say, by minimizing the calculated energy. Our estimate, based on a electronegativity data, that H_2O is roughly of polarity like $(H^{+0.4})_2O^{-0.8}$, indicates that the two terms (3) should greatly predominate over (1) in this linear combination.

As Coolidge has shown,[7] accurate calculations corresponding to (1) give results which disagree very badly with experiment. He obtains a much better, although still poor, result, by using an admixture of (1) with (3). It is to be noted, however, that contrary to our estimate of polarity $(H^{+0.4})_2(O^{-0.8})$ based on Eq. (41) of XI, Coolidge finds that the calculated energy is minimized with a wave function in which (1) still strongly predominates over (3). However, as we have seen near the end of XI, the observed electric moment of H_2O supports our estimate of the polarity, and thus indicates that the calculations made using atomic orbitals, with a minimizing condition for the energy, are not accurate enough to give a good estimate of the polarity. It seems probable, in view of the work of James and Coolidge,[5] that the use of molecular orbitals (either localized ones as in (2) or non-localized ones) could give better quantitative results than Coolidge's combination of (1) and (3).

For molecules like CH_4 and CCl_4, Pauling and Slater have used, for the carbon atom, atomic orbitals which are hybrids (mixtures) of the "natural" atomic orbitals $2s$ and $2p$. From $2s$, $2p_x$, $2p_y$, $2p_z$ they construct four equivalent hybrid atomic orbitals, which may be called tetrahedral orbitals and designated $2t$. Omitting Cl atom inner electrons, the Pauling-Slater electron configurations for the respective normal states of CH_4 and CCl_4 (symmetry T_d) may be written

$$(1s_C)^2\{(2t_C)\cdot(1s_H)\}^4,\ ^1A_1;$$
$$(1s_C)^2\{(2t_C)\cdot(3p\sigma_{Cl})\}^4(3p\pi_{Cl})^{4\times4},\ ^1A_1. \quad (4)$$

Each of the four C−H or C−Cl bonds is represented by one $2t_C$ and one $1s_H$ or $3p\sigma_{Cl}$ electron, with the axis of the $2t_C$ orbital along the C−H or C−Cl line (cf. IV of this series,[4] section 2, for a fuller description). Electron configuration (4) corresponds to homopolar C−H or C−Cl bonds; the actual, partially polar, nature of the bonds can be represented only by assuming resonance (mixing) of several other partially ionic electron configurations with (4).

In the Hund method, each bond is represented by a pair of electrons assigned to a localized

[4] R. S. Mulliken, Phys. Rev. **43**, 279 (1933): IV.
[5] R. S. Mulliken, J. Chem. Phys. **3**, 375 (1935): VI.
[6] L. Pauling, J. Am. Chem. Soc. **54**, 3570 (1932).
[7] A. S. Coolidge, Phys. Rev. **42**, 189 (1932).

molecular orbital whose form can be indicated in LCAO approximation as $(a2t_C+b1s_H)$ or $(a3p\sigma_{Cl}+b2t_C)$, with $a>b$ corresponding to the electronegativity order Cl>C>H[6]. Thus the electron configurations (omitting Cl inner electrons) may be written symbolically as

$$(1s_C)^2(2t_C+1s_H)^{2\times4},\ ^1A_1;$$
$$(1s_C)^2(3p\sigma_{Cl}+2t_C)^{2\times4}(3p\pi_{Cl})^{4\times4},\ ^1A_1. \quad (5)$$

Configurations (5) have the advantage over (4) that they can take care of any existing degree of polarity. In the writer's method, discussed for CH_4 in the next section, the rather "unnatural" mixing of $2s$ and $2p$ required in both (4) and (5) is avoided, but the advantages of (5) in regard to the description of polarity are retained. At the same time, the nonlocalized description is well adapted,—more "natural,"—for the discussion of excited and ionized states.

It is of interest to try to determine roughly the polarities of the bonds in CH_4 and CX_4 by the method already used for H_2O, based on the rough Eq. (41) of XI. Using Pauling's relative electronegativity values for C, H, I, Br, Cl and F, we get from Eq. (41) the following results for the net charge on each outer atom, in units of e: $Q_H=+0.18$, $Q_I=+0.05$, $Q_{Br}=-0.07$, $Q_{Cl}=-0.13$, $Q_F=-0.42$. The estimated internal polarities of the various molecules may then be expressed by $C^{-0.72}(H^{+0.18})_4$; $C^{-0.2}(I^{+0.05})_4$; $C^{+0.28}(Br^{-0.07})_4$; $C^{+0.52}(Cl^{-0.13})_4$; $(C^{+1.68})(F^{-0.42})_4$. Of course these estimates are very rough.

Tentatively accepting the foregoing estimates, however, one concludes that (4) can represent a fairly good approximation only for CI_4 and CBr_4. For CH_4, four equivalent electron configurations of type $C^{-1}H_3H^+$ would need to be given greatest weight in the necessary linear combination of wave functions. For CF_4, six wave functions of type $C^{+2}F_2(F^-)_2$ would be most important. If, however, we use (5), a fairly good approximation can be secured in every case with a single electron configuration.

Although a detailed discussion of molecules like CH_3X, CH_2X_2, CHX_3 will not be given here, it seems appropriate to give one or two examples of the charge distributions obtained for such molecules using Eq. (41) of XI. We apply Eq. (41) to each bond separately, and add the resulting charges at the carbon ends of the various bonds, just as we did for CH_4 and CX_4. In this way are obtained $H^{+0.18}C^{+0.03}(Br^{-0.07})_3$; $(H^{+0.18})_2C^{-0.10}(Cl^{-0.13})_2$; $(H^{+0.18})_3C^{-0.12}F^{-0.42}$. Interesting conclusions result, e.g., that in CH_3F the rather strong net negative charge on the F atom is drawn from the H atoms. Results such as these have a bearing on the interpretation of electric moment data, although, of course, one must not neglect various other factors which are or may be of comparable importance.

2. Nonlocalized Molecular Orbitals

We turn now to the method using nonlocalized molecular orbitals for shared electrons. Consider, for example, the CH_4 or CX_4 molecule (cf. V of this series[8]), with electron configuration

$$(1s_C)^2[sa_1]^2[pt_2]^6,\ ^1A_1$$
or
$$(1s_C)^2[sa_1]^2[pt_2]^6(np\pi_X)^{4\times4},\ ^1A_1. \quad (6)$$

In LCAO approximation, the bonding molecular orbitals $[s]$ and $[p_x]$,—$[p_y]$ and $[p_z]$ are similar,—are given (cf. V of this series,[8] Eqs. (5)) by

$$[s]=a(2s_C)+b\{(\alpha+\beta+\gamma+\delta)/N\}, \quad (7)$$

$$[p_x]=c(2p_x)_C+d\{(\alpha-\beta-\gamma+\delta)/N'\}, \quad (8)$$

where α, β, γ, δ refer to $1s$ orbitals of the four H atoms, or to $np\sigma$ of the four X atoms.

First let us consider CH_4. According to Pauling's scale,[6] the carbon atom is about 0.55 units more electronegative than the hydrogen atom. This, however, refers to the *average* behavior of the four valence electrons (one $2s$, three $2p$). The writer[3] has pointed out that separate electroaffinities can be given for the $2s$ and the $2p$ electrons, and these are obviously needed when we use whole-molecule orbitals like the $[s]$ and $[p]$ of CH_4 given above. The writer has estimated (reference 3, Table I) that for $2s$, carbon is 3.04 units more electronegative than hydrogen on Pauling's scale; for $2p$, 0.28 unit less electronegative than hydrogen.

In (7), the orbital $[s]$ may be regarded as of the type ϕ_{AB} of Eq. (1) or (7) of XI if we treat $(\alpha+\beta+\gamma+\delta)/N$ as a single orbital of H_4 (N=normalization factor), H_4 thus being regarded as B in AB. The results and equations

[8] R. S. Mulliken, J. Chem. Phys. **1**, 492 (1933): V.

of XI then apply. Since $a=b$ is the criterion of equal electronegativity, we may say that *if* $2s$ of C and $(\alpha+\beta+\gamma+\delta)/N$ of H_4 had equal electronegativity, then $a=b$ should be true. In a similar way, we should have $c=d$ in Eq. (8) if $2p$ of C had the same electroaffinity as $(\alpha-\beta-\gamma+\delta)$ of H_4.

In the actual case, we shall not have $a=b$ or $c=d$. Departures from these equalities will depend on differences in electroaffinity, also somewhat on Y values (cf. Eq. (19) of XI), as discussed in section 4 of XI. It is not difficult to see that the order of magnitude of H_{AB} and Y should be the same here as when a localized orbital of Hund's type is used for each bond. It appears likely, however, that Y here may be larger for the $[s]$ than for the $[p]$ orbitals, the Y for the localized orbitals then being intermediate in value.

As for the electroaffinities of $(\alpha+\beta+\gamma+\delta)/N$ and $(\alpha-\beta-\gamma+\delta)/N$ of H_4, we may use the value for the H atom as a rough approximation. The actual value is probably greater in the case of $(\alpha+\beta+\gamma+\delta)$ because of H−H bonding, and somewhat less than for free H in the case of $(\alpha-\beta-\gamma+\delta)$, where antibonding actions between H's predominate over bonding actions.

Using the electronegativity difference $(P_{C2s}-P_H=3.04)$ estimated above for carbon $2s$ relative to hydrogen $(1s)$, there can be no doubt that there is a strong inequality $a>b$, even allowing for the H−H bondings. Thus the $[s]$ orbitals must have strong polarity of C^-H^+ type, with an a/b ratio probably greater than in HF $(P_F-P_H=2.00)$. From the carbon $2p$ electronegativity (−0.28 compared with H), we conclude that c/d is not far from unity. That is, the $[p]$ orbitals are nearly homopolar. If the value −0.28 is approximately correct, there is a slight C^+H^- polarity (c/d slightly less than 1).

In terms of homopolar strength, the bonding per electron is then probably stronger for the $[p]$ than for the $[s]$ electrons. Nevertheless, especially if Y is considerably larger for $[s]$ than for $[p]$, the former may give rather strong homopolar bonding. There is also more or less heteropolar bonding. One might think to divide the latter between the $[s]$ and $[p]$ orbitals, but such a division would probably be meaningless. In fact in the last analysis the energy of formation of a molecule from its atoms cannot be assigned exclusively, nor even more than in a very rough way, to the "bonding electrons" alone, no matter what type of electron configuration is used. Nevertheless the presence of the "bonding electrons" or of the heteropolar character is decisive for the stability of the molecule.

If we make use of electroaffinity and other data in studying the $[s]$ and $[p]$ orbitals of CX_4 and other similar molecules RA_4 (e.g., SiH_4, SiX_4, NH_4^+, BF_4^-, $SO_4^=$, ClO_4^-), we find interesting variations in the polarity and in the relative bonding effects of $[s]$ and $[p]$. At one extreme is the case where the $[s]$ orbitals have very strong R^-A^+ polarity and so are practically unshared *ns* electrons of the central atom *R*, while the $[p]$ orbitals are nearly homopolar and strongly bonding (probable example ClO_4^-, and to a less complete extent CI_4 (cf. I of this series[9])). In such a case the *four* C−H bonds of classical chemical valence theory are provided almost entirely by *three* pairs of $[p]$ electrons, the total bonding of the group $[p]^6$ being directed, however, equally toward all four A's (cf. I of this series).

At the other extreme, which occurs when A is very electronegative relative to R, we have a and b nearly equal so that the $[s]$ orbitals give strong homopolar bonding. At the same time the $[p]$ orbitals have very strong R^+A^- polarity $(c\ll d)$ and so belong predominantly to the outer atoms A and contribute only a little to the homopolar part of the R−A bonding (example, SiF_4). In such a case the total bonding is about as much heteropolar as homopolar, or in other words is about half-way between these two ideal cases.

The foregoing discussion tends to indicate that, contrary to a suggestion of Pauling and Slater, the high stability of tetrahedral molecules and ions RA_4 is not due particularly to an ability of $s-p$ mixed (tetrahedral) atomic orbitals to form especially strong homopolar bonds. For as we have just seen, the types RA_4 range over a variety of cases from one where there is strong homopolar p binding but hardly any homopolar s binding to one where the roles of s and p are

[9] R. S. Mulliken, Phys. Rev. **40**, 55 (1932): I.

reversed; at the same time the heteropolar contribution to the binding varies greatly. Approximate calculations of Van Vleck,[10] using various types of electron configurations (Slater-Pauling, LCAO molecular orbital, and ionic), also indicate that the stability of the tetrahedral arrangement is not specially connected with the simultaneous presence and mixing of s and p atomic orbitals.

Instead of this, the foregoing discussion strongly suggests, as has been pointed out without the present detailed justification in earlier papers (I, II, and especially V, p. 501 of this series[8]), that the exceptional chemical stability of tetrahedral RA_4 types is due to an unusually favorable close packing of positive charges and negative electricity which is possible for this rather high type of symmetry. In crystal structure the great importance of coordination number in relation to stability is well recognized. A similar effect may well operate here. It appears that the form RA_4 (neutral or charged) is favored whenever it can be attained without sacrificing the even more important stability criterion (cf. II of this series, sections 3 and 7)[11] that the electrons surrounding each nucleus constitute from the latter's point of view a set of closed shells of relatively low energy.

We return now to a consideration of degrees of heteropolarity in molecules RA_4. The total strength of the R−A bonds can, at least roughly, be divided into a homopolar and a heteropolar part. The homopolar strength is approximately proportional to the quantity H_{AB} or Y of Eq. (19) of XI, which is usually approximately proportional to the "overlapping integral" $S=\int \phi_A\phi_B dv$. The heteropolar strength can be roughly gauged from a knowledge of R−A distances and of the net charges Q assignable to the atoms R and A. These charges can most conveniently be determined by the method of section 1, based on Eq. (41) of XI, with the use of localized molecular orbitals for each bond.

The same net charges should, however, presumably be obtainable by applying Eq. (41) of XI using nonlocalized molecular orbitals and summing the effective atomic charges corresponding to all the electrons assigned to such orbitals. Let us consider CCl_4 and CF_4 as examples. In order to get Q_C, we should obviously take

$$Q_C=(Q_C \text{ for } [s]) \text{ plus } 3\times(Q_C \text{ for } [p]),$$

since Q_A of Eq. (41) of XI gives the net charge on atom A due to *one pair* of electrons distributed between A and another atom, or group of atoms in the present application, called B. With the usual reservations, somewhat enhanced here because the quantity Y may differ very considerably for $[s]$ and $[p]$, we may use Eq. (41).

From Eq. (41), we find

$$CCl_4: Q_C=-0.51+3\times0.37=+0.60;$$
$$CF_4: Q_C=-0.32+3\times0.51=+1.21.$$

Thus we get net polarities $(C^{+0.60})(Cl^{-0.15})_4$ and $(C^{+1.21})(F^{-0.30})_4$ as compared with the results $(C^{+0.52})(Cl^{-0.13})_4$ and $(C^{+1.68})(F^{-0.42})_4$ obtained in section 1. The lack of exact agreement is probably not due entirely to our use of different approximate wave functions in the two cases, but partly if not largely to the rough form in which we have developed the theory. At least part of the discrepancy is obviously due to our use of the two-term Eq. (41) with constant coefficients. It seems hardly worth while to consider the matter here in more detail. Besides, it seems clear that the results obtained by the method of section 1 should be at least approximately applicable here, and they are probably more accurate than those calculated here by applying Eq. (41) to $[s]$ and $[p]$ separately and summing.

We turn now to another problem often encountered in studying the forms of nonlocalized molecular orbitals. As was mentioned in section 4 of XI, coefficient ratios such as a/b in any ϕ_{AB} depend, except in the case $a=b$, not only on relative electronegativities, but also on bond angles in case these are not fixed by the assumed symmetry. In the tetrahedral type RA_4 discussed above, the bond angles are fixed by the symmetry so that we did not need to consider them.

In some cases the H_{AB}'s and Y's of different molecular orbitals depend on bond angles in a way which is important for our qualitative treatment. As an example, we may consider the

[10] J. H. Van Vleck, J. Chem. Phys. **1**, 177, 219 (1933); **2**, 20, 297 (1934).
[11] R. S. Mulliken, Phys. Rev. **41**, 49 (1932): II.

bonding orbitals of H_2O. The normal state electron configuration[12] is

$$1s^2(2sa_1)^2[yb_2]^2[za_1]^2(2p_xb_1)^2,\ ^1A_1, \qquad (9)$$

all the orbitals being essentially nonbonding O atom orbitals except the two O−H bonding orbitals $[y]$ and $[z]$. These may be approximated (cf. IV of this series,[4] Eqs. (8)) by

$$[y]=a(2p_y)_O+b\{(\alpha-\beta)/N\}, \qquad (10)$$

$$[z]=c(2p_z)_O+d(\alpha+\beta)/N'\}; \qquad (11)$$

the z axis bisects the HOH angle, the y axis lies in the HOH plane, and α and β refer to $1s$ orbitals of the two H atoms, with the α nucleus located in the region of positive y.

Now if O and H had equal electroaffinity (more rigorously, if $2p$ of O had the same electroaffinity as $\alpha-\beta$ and $\alpha+\beta$ of H−H), then we should have $a=b$ and $c=d$. Since actually O is much more electronegative than H, we have $a/b>1$ and $c/d>1$. We do not, however, in general have $a/b=c/d$. This can easily be seen qualitatively by considering extreme values 180° and 0° for the HOH angle ϕ.

For $\phi=180°$, the directions x and z become equivalent, both being perpendicular to the line HOH which is now the y axis; the symmetry now becomes $D_{\infty d}$. Here $[z]$ becomes pure $2p_z$ of O, i.e., $c=1$, $d=0$ in (11), and $2p_z$ and $2p_x$ become a degenerate pair of nonbonding orbitals which may be called $2p\pi_u$. The result $c=1$, $d=0$, i.e., $c/d=\infty$, shows (cf. Eq. (16) of XI) that $(H_{AB}-SW)=0$ for $[z]$ when $\phi=\pi$. At $\phi=\pi$, H_{AB} and S both vanish together, as is easily seen from symmetry considerations. The quantity $Y=H_{AB}-SX$, which is nearly the same as $H_{AB}-SW$, also approaches zero as $\phi\rightarrow\pi$. At the same time that $-H_{AB}$, S, and $-Y$ approach zero for $[z]$, they can be shown to approach a maximum value for $[y]$, which becomes a double-ended bonding orbital of σ_u type. The energy is then very considerably lower (I greater) for $[y]$ than for $[z]$.

For $\phi=0$ the roles of $[y]$ and $[z]$ are reversed. The symmetry is $C_{\infty v}$. Here $[y]$ becomes pure $2p_y$ ($a=1$, $b=0$) and is degenerate with $2p_x$, the two being classifiable as $2p\pi$, while $[z]$ has maximum bonding and maximum I, and is of type σ. It is easily seen that as ϕ goes from 0 to π, b/a goes up from zero to a maximum value, while d/c descends from a maximum value to zero, each varying roughly in proportion to Y of $[y]$ or $[z]$, respectively. It is evident that for some angle between zero and π, $a/b=c/d$ must hold; also somewhere H_{AB}, S, and Y must be equal for $[y]$ and $[z]$; and somewhere I must be the same for $[y]$ as for $[z]$.

These relations, it can be shown,[13] would all nearly hold for $\pi/2$ if we could entirely neglect all terms in W of Eq. (11) of XI which in any way involve both H atoms (either their orbitals, or their potentials) simultaneously. In this case we should have $b/a>d/c$ for the actual H−O−H angle of about 105°, and $-H_{AB}$, S, $-Y$, and I would be somewhat larger for $[y]$ than for $[z]$, as was estimated (in the case of I) in V of this series.[8] Allowance must, however, be made for the H−H interactions, which tend to lower the energy of $[z]$ considerably relative to $[y]$, since the former involves H−H bonding, the latter H−H antibonding. Hence actually for $\pi/2$, $[z]$ should be lower in energy than $[y]$, and the critical angle at which the $[y]$ and $[z]$ curves of I against ϕ cross must exceed $\pi/2$. Quite possibly $[y]$ and $[z]$ are nearly degenerate for the actual angle of about 105°.

The methods exemplified in this paper for qualitatively or semiquantitatively determining polarities in molecular orbitals will be used continually, explicitly or implicitly, in the papers of this series.

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[12] R. S. Mulliken, J. Chem. Phys. **3**, 506 (1935): VII.

[13] The writer is indebted to Professor Van Vleck for calling his attention to this point. The proof is easily obtained using Eq. (11) of XI; cf. also F. Hund, Zeits. f. Physik **73**, 1 (1931).

Incomplete Atomic Arrangement in Crystals

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γ-Fe_2O_3, γ-Al_2O_3 and the oxide obtained by the electrolytical oxydation of Al (γ'-Al_2O_3) are averaged structures with regard to the cations. Both the γ and γ' oxides have the same oxygen-lattice but there is a distinct difference in the degree of incomplete arrangement of the cations. γ'-Al_2O_3 and γ-Al_2O_3 (Fe_2O_3) are intermediate cases between the amorphous state and the completely arranged state.

CRYSTAL structures in which part of the atoms (ions) are distributed statistically (averaged structures) have been described for a few compounds. Thus, in $Li_2O.Fe_2O_3$, the Li and Fe ions are distributed at random over the cation positions of the simple NaCl-arrangement.[1] In a number of compounds with spinel structure, e.g. Mg_2GaO_4, the Ga-ions and half of the Mg-ions take equivalent positions, with an averaged distribution ("variate atom equipoints").[2] An interesting type of averaged structure is shown by the high temperature modification of Ag_2HgI_4[3] and related compounds, since here we deal with an averaged distribution of vacant positions and cations over a number of definite lattice positions.

Striking cases of a statistical atomic arrangement, partially differing from the types mentioned above, were found to exist with a number of oxides A_2O_3 and will be discussed in the present note. Crystallographical details, to be published in Zeits. Krist., will be omitted.

We examined the closely related compounds γ-Al_2O_3 and γ-Fe_2O_3, the instable cubic modifications of these oxides. From density relationships and considerations concerning ionic radii we believed both the structure proposed by Welo and Baudisch[4] and the one given by Thewlis[5] to be incorrect. γ-Fe_2O_3 and γ-Al_2O_3 were found to have a face-centered oxygen lattice; the unit cell contains 32 oxygen ions. The cations are distributed in a way statistically over the 8+16 spinel positions in such a way that per unit cell on the average $21\frac{1}{3}$ cations and $2\frac{2}{3}$ vacant positions are distributed over the 24 definite positions.

Besides, we studied the structure of the Al_2O_3 obtained by the electrolytical oxidation of aluminium. This Al_2O_3 is closely related with γ-Al_2O_3 but in its x-radiograms some of the lines of γ-Al_2O_3 fail.[6] We have called this oxide γ'-Al_2O_3. This γ'-Al_2O_3 has a face-centered arrangement of the oxygen ions too. The unit cell contains 4 oxygen ions and on the average $2\frac{2}{3}Al^{3+}$ ions. These cations are distributed in a way statistically over 12 positions, *viz.* 8 in which the Al^{3+} ion is surrounded by $4O^{2-}$-ions and 4 in which the coordination number is 6; the former positions contain about 30 percent, the latter about 70 percent of the cations.

Thus γ-Fe_2O_3, γ-Al_2O_3 and γ'-Al_2O_3 belong to the large class of compounds with a cubic close packed anion lattice, containing the smaller cations in the interstices between the anion spheres. Such a close packing contains, per unit cell of 4 anions, 8 tetrahedron holes (surrounded by 4 anions) and 4 octahedron holes. In Li_2O the tetrahedron holes are all occupied (CaF_2-type), in MgO, FeO, etc., and the $Li_2O.Fe_2O_3$ mentioned above, the octahedron holes are filled (NaCl-type), the unit cell containing in both cases 4 oxygen ions.

It is convenient to describe the structure of AgI, Ag_2HgI_4 (α and β) in a similar way. In these compounds too the unit cell contains $4I^-$-ions according to a face centered lattice. In AgI half of the tetrahedron interstices are occupied in such a way that the cubic symmetry is maintained. In Ag_2HgI_4 one of these positions

[1] E. Posnjak and T. F. W. Barth, Phys. Rev. **38**, 2234 (1931).
[2] T. F. W. Barth and E. Posnjak, Zeits. f. Krist. **A82**, 325 (1932); cf. also F. Machatschki, ibid. **82**, 348 (1932).
[3] J. A. A. Ketelaar, Zeits. f. Krist. **A87**, 436 (1934); Zeits. f. physik. Chemie **B26**, 327 (1934).
[4] L. A. Welo and O. Baudisch, Phil. Mag. (6) **50**, 399 (1925).
[5] J. Thewlis, Phil. Mag., (7) **12**, 1089 (1931).
[6] W. G. Burgers, A. Claassen and J. Zernike, Zeits. f. Physik **74**, 593 (1932).

is vacant; however, the three remaining positions can be occupied in different ways. In β-Ag_2HgI_4 (low temperature modification) the cations take three definite positions, which leads to a tetragonal (pseudocubic) symmetry;[7] in α-Ag_2HgI_4 the three cations are distributed statistically over the 4AgI positions, and the symmetry is again a cubic one.

Now in γ-Al_2O_3, γ-Fe_2O_3 and γ'-Al_2O_3 the cations are distributed over both tetrahedron and octahedron holes.

γ-Fe_2O_3 and γ-Al_2O_3 can be derived from the spinel structure; this structure involves a larger cell, containing 32 oxygen ions per unit. In normal spinels the cations are distributed according to a regular arrangement over 8 tetrahedron holes and 16 octahedron holes. (The unit cell contains 64 tetrahedron positions and 32 octahedron positions.) In the γ-oxides a number of these 24 positions are vacant (preferably octahedron positions), on the average $2\frac{2}{3}$ per unit cell. The averaged structures of the γ-oxides and of α-Ag_2HgI_4 are therefore of a similar type. There is a partial arrangement of the cations since only part of the available interstices are used. A number of cations and vacant places are distributed at random over these definite positions.

However, a distinct difference between the γ-oxides and α-Ag_2HgI_4 exists. The latter compound has a transition point: at 50° the averaged structure is converted to the regular arrangement of β-Ag_2HgI_4 (low temperature modification). This transition indicates that the cations in α-Ag_2HgJ_4 must have a large mobility, and move more or less freely in the lattice. The α-modification has actually a high electrolytical conductivity[8] and is a cation conductor. Accordingly there is an intimate connection between this conductivity and the averaged structure: the cations (especially the Ag^+ ions) jump frequently from one AgI-position to another, leaving each of them on the average $\frac{1}{4}$ of the time vacant. One could say that the Ag^+ ions, though partially arranged according to AgI-positions, are in a kind of *fluid state* in these lattices. If the temperature is lowered to the transition point, the Ag^+-ions "crystallize" and take definite positions.

γ-Fe_2O_3 has no appreciable electrolytical conductivity in its existence region.[8] The probability of a jump from one spinel position to another is obviously negligible. The case is therefore different from that of α-Ag_2HgJ_4. The incomplete arrangement of the cations is not caused by their thermal agitation but by the impossibility or improbability of a simple arrangement in the cubic close packed O^{--}-lattice. It is comparable with a partially *amorphous state* of these cations.

In γ'-Al_2O_3 the Al-ions are distributed quite statistically over all interstices of the lattice; the only restriction is that averaged 70 percent of the Al-ions have chosen an Al^6 position (octahedron hole), 30 percent an Al^4 position. The arrangement of the cations is still more incomplete than in the γ-oxides, and the partial (spinel) arrangement of the latter fails. Only small deviations from the statistical distribution are present, i.e., the cations are practically entirely in an amorphous state.[9] In this respect, γ'-Al_2O_3 is actually one of the most striking averaged structures so far found.

γ' and γ-Al_2O_3 can be considered as intermediate cases between the amorphous and the totally arranged state. In γ'-Al_2O_3 only the anions are arranged regularly. The second step from the amorphous to the completely arranged state can be realized by a careful heating of γ'-Al_2O_3 (900°C). Then γ-Al_2O_3 is formed, and a partial arrangement of the cations occurs in the way described which leads to a spinel arrangement with a larger unit cell. A *complete* arrangement of the cations is finally realized when γ-Al_2O_3 is heated above 1000°. Then α-Al_2O_3 is formed, i.e., the cubic close packed oxygen lattice is transformed into a hexagonal close packing. A simple complete arrangement of cations and anions in a ratio 2 : 3 is, for geometrical reasons, obtained easily in the latter class of symmetry: α-Al_2O_3 has a rhombohedral cell with $4Al^{3+}$ and $6O^{--}$, in which the cations occupy 2/3 of the octahedron holes.

[7] J. A. A. Ketelaar, Zeits. f. Krist. **80**, 190 (1931).

[8] H. Sachse, Zeits. f. Physik **70**, 539 (1931).

[9] An example of a "wholly fluid" state of the cations is probably α-AgI. However, the structure given recently by L. W. Strock, Zeits. f. physik. Chemie **B25**, 441 (1934), seems to be not quite clear.

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge (\$3.00 per page) will not be made and no reprints will be furnished free.

The Raman Spectra of Dioxane

On occasion of an investigation of Raman spectra of oxomium association compounds we studied the Raman spectra of dioxane. The results obtained show some discrepancies from those of Villars,[1] who probably used a set of less aperture and worked without light-filter. Dioxane, prepared from ethylene-glycol according to Favorsky,[2] and having the boiling-point at 96–102°C was investigated in a Raman apparatus described elsewhere.[3] The exposure was one hour. We obtained 29 Raman lines while Villars obtained 21, and all the lines of Villars were reproduced except 20,214 cm^{-1}(00). The spectra taken with a quinine filter according to Warburg and Nezelein with an exposure of two hours show some errors in the readings of Villars, who found the following Raman frequencies (in cm^{-1}):

291(0)(*i,k*); 434(00)(*e*); 519(0)(*e*); 837(4)(*e,i,k*); 1117(1)-(*g,i,k*); 1214(1)(*k*); 1442(2)(*e,k*); 2720(00)(*e,k*); 2864(3)-(*e,i,k*); 2967(3)(*e,i,k*).

Instead of these frequencies we obtained the following: 427(3)(*e,k*); 487(3)(*e,k*); 836(10)(*e,f,i,k*); 940(2)(*e,f,k*); 1017(5)(*e,k*); 1115(5)(*e,k*); 1213(3)(*e,k*); 1306(5)(*e,k*); 1450(6)(*e,f,k,m*); 2862(10)(*e,k*); 2971(10)(*e,k,p,q*).

It is interesting to note the close resemblance between the Raman spectra of dioxane and of ether. We obtained for the latter the following frequencies, which do not largely differ from the data of Bär.

440(5)(*e,f,g,i,k,m*); 497(*i*)(*e,i,k*); 843(8)(*e,f,i,k*); 928(3)-(*e,i,k*); 1152(1)(*k*); 1276(2)(*e,k*); 1456(5)(*e,f,g,k,m*); 2694-(4)(*k*); 2807(5)(*k,g*); 2872(10)(*e,k,g*); 2935(10)(*e,k,g*); 2983(10)(*e,k,o,p,q*). We did not find the line 2730(1) of Bär and observed a new line 497(1).

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[1] Villars, J. Am. Chem. Soc. **52**, 4612 (1930); K. W. Kohlrausch, *Der Smekal-Raman Effect*, p. 338.
[2] Favorsky, J. Russ. Chem. Soc. **38**, 741 (1906) (Russian).
[3] Syrkin und Wolkenstein, Acta Phys. Chim. URSS **2**, 303 (1935).
[4] Warburg and Nezelein, Zeits. f. physik. Chemie **106**, 191 (1923).
[5] K. W. F. Kohlrausch, reference 1, p. 311.

Surface Ionization of Potassium Iodide on Tungsten

It has been shown by Rodebush and Henry[1] that positive ions are formed when molecular rays of alkali halides strike a hot oxygen-coated tungsten surface. We have made a further study of this phenomenon; in particular we have observed, as a function of the surface temperature, the positive ion current obtained when a constant ray of KI molecules struck a tungsten filament, first oxygen-coated and then stripped of its oxygen (by flashing at a high temperature). In the region of temperature in which the oxygen layer is stable the positive ion current was constant. A similar constancy was observed by Langmuir and Kingdon[2] for alkali metals on an oxygen-coated surface, and was interpreted by them as indicating complete ionization.

When the wire was flashed and the oxygen removed, the positive ion current was found to be lower at all temperatures than before flashing, and was observed to decrease with increasing temperature. This behavior after flashing was the same as that reported by the authors[3] for potassium atoms. The fact that metal and salt showed the same behavior suggests that the essential ionization process in both cases is the same: namely, the ionization of a potassium atom on the surface. This would imply a preliminary dissociation of the adsorbed salt molecule into atoms on the surface. Making this assumption, we have calculated values of the ratio of the numbers of potassium ions to potassium atoms evaporating from the clean wire at temperatures in the region 1700° to 2200°K.

It has been shown theoretically[2] that in the case of potassium atoms the following relation should hold:

$$\log_{10}\frac{i_+}{i_a}=\log_{10}C+\frac{(\phi-I)\epsilon}{2.303k}\cdot\frac{1}{T},$$

where i_+/i_a is the ion-atom ratio, ϕ is the work function of the surface, I is the ionization potential of the atom, and C is a constant for a given surface and atom. When a plot of the logarithm of the ion-atom ratio for the salt case was made against $1/T$, a straight line was obtained whose slope and intercept were found to agree within experimental error with those observed[3] for potassium metal. This agreement confirms the suggested mechanism.

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[1] Rodebush and Henry, Phys. Rev. **39**, 386 (1932).
[2] Langmuir and Kingdon, Proc. Roy. Soc. **A107**, 61 (1925).
[3] Copley and Phipps, Phys. Rev. **45**, 344 (1934).

Energy Formula and Potential Distribution of Diatomic Molecules*

Taking as general expression of a diatomic molecular potential $V(r)$ the following one,

$$\left.\begin{aligned} V&=-D+D\xi^2, \quad 1-\xi=\frac{(1+a)(1+c)}{1+b}\,\frac{x+b}{(x+a)(x+c)},\\ x&=e^{(1+k)\rho}, \quad \frac{1}{1+k}=\frac{1}{1+a}+\frac{1}{1+c}-\frac{1}{1+b},\\ \rho&=[h\nu_e/2(B_eD)^{\frac{1}{2}}](r-r_e)/r_e, \end{aligned}\right\} \tag{1}$$

r_e being the equilibrium distance of the atoms and D, B_e and $h\nu_e$ well-known spectroscopic constants, the energy formula may be expressed as follows,

$$\left.\begin{aligned} 1-\left(-\frac{E}{D}\right)^{\frac{1}{2}}&=\frac{h\nu_e}{2D}(n+\tfrac{1}{2})+\frac{A(h\nu_e/2D)^2(n+\frac{1}{2})^2}{1-\varkappa(h\nu_e/2D)(n+\frac{1}{2})},\\ A&=\tfrac{1}{2}(1-a_2), \quad \varkappa=1-a_2+\frac{a_2-a_4}{1-a_2}, \end{aligned}\right\} \tag{2}$$

a_2 and a_4 being coefficients in the expansion of $d\rho/d\xi$ in power series of ξ,

$$d\rho/d\xi=1+a_1\xi+a_2\xi^2+a_3\xi^3+a_4\xi^4+\cdots. \tag{3}$$

The rotational constant B depends upon the vibrational quantum number n in the following way,

$$\left.\begin{aligned} B&=B_e-\alpha(n+\tfrac{1}{2})-\alpha_2(n+\tfrac{1}{2})^2-\cdots\\ \alpha/B_e&=\frac{h\nu_e}{2D}\left[3a_1\left(\frac{2(B_eD)^{\frac{1}{2}}}{h\nu_e}\right)-3\left(\frac{2(B_eD)^{\frac{1}{2}}}{h\nu_e}\right)^2\right],\\ \alpha_2/B_e&=\left(\frac{h\nu_e}{2D}\right)^2\left[\left(\frac{15}{4}a_3-2a_1a_2\right)\left(\frac{2(B_eD)^{\frac{1}{2}}}{h\nu_e}\right)\right.\\ &\quad-\left(3a_2+\frac{45}{8}a_1^2\right)\left(\frac{2(B_eD)^{\frac{1}{2}}}{h\nu_e}\right)^2+15a_1\left(\frac{2(B_eD)^{\frac{1}{2}}}{h\nu_e}\right)^3\\ &\quad\left.-\frac{15}{2}\left(\frac{2(B_eD)^{\frac{1}{2}}}{h\nu_e}\right)^4\right]. \end{aligned}\right\} \tag{4}$$

The coefficients a_1, a_2, a_3, a_4, may be derived from the expression

$$\left.\begin{aligned} \rho&=\frac{1}{1+k}\log\frac{1}{1-\xi}\left\{1+k\xi-\frac{2k_1k_2(1+k)\xi^2}{1+(k_1+k_2+2k_1k_2)\xi+\sqrt{[1+(k_1+k_2+2k_1k_2)\xi]^2-4k_1k_2(1+k_1)(1+k_2)\xi^2}}\right\},\\ k_1&=\left(\frac{1}{1+b}-\frac{1}{1+a}\right)(1+k), \qquad k_2=\left(\frac{1}{1+b}-\frac{1}{1+c}\right)(1+k). \end{aligned}\right\} \tag{5}$$

If now this energy formula can be adjusted to the observed vibrational energy levels of a molecule, the coefficients a_2 and a_4 are already given. The coefficient a_1 may easily be found from the first order dependance of B upon the quantum number n. Thus the constants of the potential curve, k, k_1 and k_2, or, a, b and c are defined and may be calculated from a_1, a_2 and a^4 and so we have an analytical expression of the potential distribution of the molecule.

In Fig. 1 some potential curves are given, the solid curve being the well-known potential curve given by Morse.[1] With the same curvature and the same asymmetry at the minimum point the dotted curves are narrower in the upper part, thus raising progressively the upper energy levels.

In Fig. 2 quite another variation possibility of the curves is illustrated, the energy formula being unaltered and only the symmetry of the curves being changed.

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Chr. Michelsens Institutt,
Bergen,
June, 1935.

* Publikasjoner fra Chr. Michelsens Institutt Nr. 50.

[1] P. M. Morse, Phys. Rev. **34**, 57 (1929).

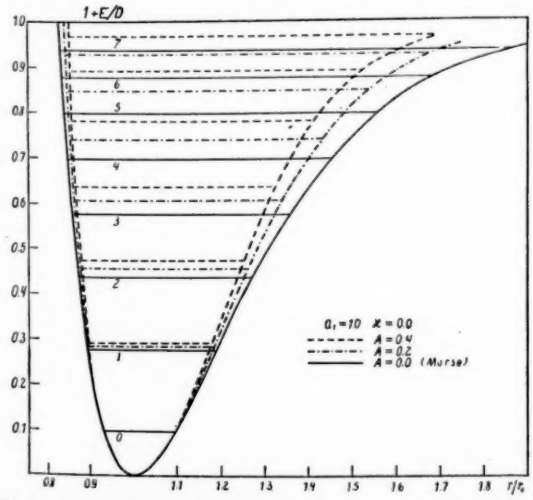

FIG. 1. Dependance of the upper levels of the narrowness of the potential curves.

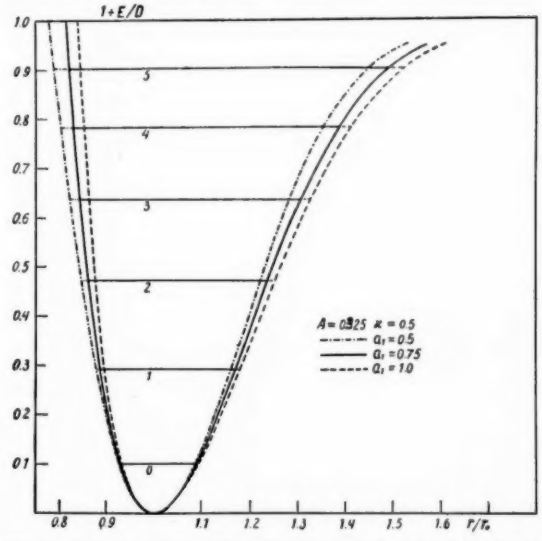

FIG. 2. Potential curves with different asymmetry but with identical energy levels.

The Oxidation of the Ferrocyanide, Arsenite and Selenite Ions by the Irradiation of Their Aqueous Solutions with X-Rays

Gas-free solutions containing the ferrocyanide ion were irradiated with x-rays and were analyzed for hydrogen and oxygen; and for the ferrocyanide ion by potentiometric titration with potassium permanganate. The ferrocyanide is oxidized to ferricyanide and hydrogen is liberated in the equivalent amount. The number of equivalents oxidized is independent of the concentration, from 0.1 to 100.0 millimoles per 1000 cc and of the hydrogen ion concentration from $pH=2.0$ to 11.0, and equals 1.10 microequivalents per 1000 r per 1000 cc. Solutions of arsenite and selenite, which were studied over the same range of concentration and of pH, were transformed by irradiation to arsenate and selenate, respectively, with the production of hydrogen, and the number of equivalents transformed was the same as in the case of the ferrocyanide. Similar results were previously obtained for the nitrite ion.[1]

It is concluded that all these transformations are due to one particular type of x-ray activated water molecule, produced in the amount of 0.55 micromole per 1000 r per 1000 cc. The reactions may be represented as follows:

$$2Fe(CN)_6^{----}+(H_2O)_{act.}+H_2O=2Fe(CN)_6^{---}+2OH^-+H_2$$
$$AsO_3^{---}+(H_2O)_{act.}=AsO_4^{---}+H_2$$
$$SeO_3^{--}+(H_2O)_{act.}=SeO_4^{--}+H_2$$
$$NO_2^-+(H_2O)_{act.}=NO_3^-+H_2.$$

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August 14, 1935.

[1] H. Fricke and E. J. Hart, J. Chem. Phys. **3**, 365 (1935).

The Decomposition of Water by X-Rays in the Presence of the Iodide or Bromide Ion

We have earlier found[1] that no decomposition of water results from its irradiation with x-rays. We now find that decomposition does occur when the water is irradiated in the presence of either the iodide or the bromide ions.

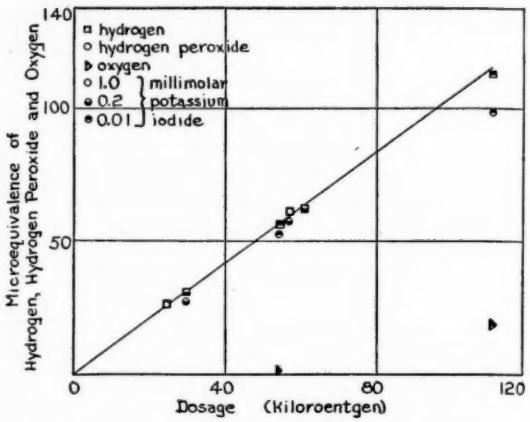

FIG. 1. Decomposition of water in the presence of the iodide ion at $pH=3.0$. Due to the decomposition of the primarily formed hydrogen peroxide, oxygen is produced at the highest dosage.

The action of these ions is catalytic inasmuch as we have been unable to detect any change in their concentrations as a result of the irradiation. In acid solutions, in the presence of sulfuric acid at $pH=3$ and 4, hydrogen and hydrogen peroxide are produced in the amount of 0.55 micromole per 1000 cc and per 1000 r of dosage. In unbuffered solutions or in the presence of sodium hydroxide at $pH=11.0$, the same amount of hydrogen is produced, but instead of hydrogen peroxide, the equivalent amount of oxygen is obtained. The decomposition is independent of the halide ion concentration from 1.0* to 0.01 millimole per liter while for lower concentrations the decomposition decreases. Fig. 1 shows the results obtained for potassium iodide at $pH=3$.

In the presence of the chloride ion, this catalytic decomposition of the water is not obtained.

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[1] H. Fricke and E. R. Brownscombe, Phys. Rev. **44**, 240 (1933).
* For higher concentrations of the potassium iodide, free iodine is formed as a result of the irradiation.